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"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. l. Not.*

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VOL. XXXVIII.—FIFTH SERIES.

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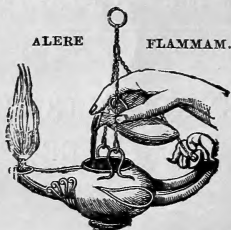
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“Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem.”—*Hugo de S. Victore.*

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—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condât,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*



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[FIFTH SERIES.]

JULY 1894.

I. *The Attraction of Unlike Molecules.*—I. *The Diffusion of Gases.* By WILLIAM SUTHERLAND\*.

IN my previous papers on the laws of molecular force the attractions of like molecules have been under consideration, and the results seemed to indicate that the laws of the attractions of unlike molecules would not be difficult to ascertain. With the hope of determining the general law of attraction of any two molecules, I adopted two methods as being at present available for giving values of the attractions of unlike molecules, namely, that of the Diffusion of Gases and that of the Surface-Tension of Mixed Liquids. Both methods have led to the same result, viz., that if the attraction between two molecules  $M_1$  of mass  $m_1$  at distance  $r$  apart be denoted by  $3A_1m_1^2/r^4$ , and that between two molecules  $M_2$  by  $3A_2m_2^2/r^4$ , then the attraction between an  $M_1$  and an  $M_2$  is

$$3\sqrt{A_1A_2}m_1m_2/r^4,$$

or the attraction of two unlike molecules is equal to the square root of the product of the attractions of the corresponding like molecules at the same distance apart. As the expression  $3A_1m_1^2$  for two like molecules can be split into two parts  $\sqrt{3A_1}m_1$ , the general law of the attraction of any two molecules, like or unlike, can be stated thus:—Any two molecules attract one another with a force inversely proportional to the fourth power of the distance between them

\* Communicated by the Author.

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and directly proportional to the product of the parameters  $\sqrt{3Am}$  characteristic of each. Although the parameter is written in the form  $\sqrt{3Am}$  apparently involving the mass  $m$  it will be shown that  $\sqrt{3Am}$  is independent of the mass  $m$  but is a function of the size of the molecule; it would therefore be better denoted by a single symbol  $a$ , so that the attraction between any two molecules  $M_1$  and  $M_2$  is  $a_1a_2/r^4$ , or between two  $M_1$  is  $a_1^2/r^4$ , the parameter  $a$  being a function of the size of the molecule but not directly of its mass. Thus, with  $Gm_1m_2/r^2$  to denote the gravitational attraction of two molecules  $M_1$  and  $M_2$ , the general expression for the force between them is

$$Gm_1m_2/r^2 + a_1a_2/r^4.$$

The dependence of the coefficient of diffusion of two gases on the attraction between their molecules was indicated in general terms in a recent paper on the Viscosity of Gases and Molecular Force (Phil. Mag., Dec. 1893). In that paper it was shown that in those parts of the kinetic theory of gases which depend on the number of encounters of a molecule per second (or, in other words, on its mean free path), the effect of molecular force cannot be neglected as of only secondary importance; it is fundamental. Thus the complete expression for the coefficient of diffusion of two gases will involve the attractions between their molecules in a manner now to be established; but as the kinetic theory of the diffusion of gases, even when simplified by treating the molecules as forceless, is in a little confusion (there being at least three forms of expression for the diffusion-coefficient in the field), it may be desirable to recapitulate briefly the theories of the diffusion of forceless molecules from the three points of view.

The first in time is that of Stefan, accepted by Maxwell; the second is O. E. Meyer's, given in his book on the 'Kinetic Theory of Gases;' and the third is that of Tait (Trans. Roy. Soc. Edin. xxxiii.), who has treated the diffusion of gases rather elaborately.

Stefan's theory is this:—If two gases are diffusing into one another, then at any point one has a general velocity  $\alpha_1$  in one direction, and the other a velocity  $\alpha_2$  in the other, the density of the first diminishes in the direction of  $\alpha_1$ , of the second in that of  $\alpha_2$ . Consider, then, an element of the first of section unity and length  $\delta x$  in the direction of  $\alpha_1$ : the partial pressure due to its molecules at one end is  $p_1$ , and at the other  $p_1 + \delta x dp_1/dx$ , so that there is a driving pressure  $\delta x dp_1/dx$  which is resisted by a resistance like friction offered by the other gas in the length  $\delta x$ , which may be denoted by

$R \delta x$ , and then any acceleration of the element of the first gas is due to the force  $\delta x (dp_1/dx - R)$ , but this acceleration can be neglected in comparison with either  $\delta x dp_1/dx$  or  $R \delta x$ , and we have

$$R = dp_1/dx. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$R$  has now to be evaluated ; it is the resistance offered by the molecules of the two sets in unit volume at  $x$  to one another's motion. Let  $\nu$  be the number of encounters per second between  $n_1$  molecules of the first set in unit volume and  $n_2$  of the second, and let  $\mu$  be the average value of the momentum communicated when a molecule of the first set with velocity  $\alpha_1$  collides with one of the second with velocity  $\alpha_2$  in the opposite direction, then

$$R = \nu \mu.$$

If  $a_1$  and  $a_2$  are the radii of the molecules of the two sets treated as spheres, and  $3\kappa_1^2/2$  and  $3\kappa_2^2/2$  are their mean square velocities, then (see for instance Tait, Trans. Roy. Soc. Edin. xxxiii.)

$$\nu = 2n_1n_2(a_1 + a_2)^2\pi^{\frac{1}{2}}(\kappa_1^2 + \kappa_2^2)^{\frac{1}{2}},$$

$$\mu = \frac{2}{3} \frac{m_1m_2}{m_1 + m_2} (\alpha_1 + \alpha_2).$$

Now in diffusion the pressure remains constant, so that as many molecules of one sort pass in one direction as of the other in the other, or  $n_1\alpha_1 = n_2\alpha_2$ , and accordingly

$$R = \frac{4}{3} n_1n_2(a_1 + a_2)^2\pi^{\frac{1}{2}}(\kappa_1^2 + \kappa_2^2)^{\frac{1}{2}}\alpha_1 \left(1 + \frac{n_1}{n_2}\right) \frac{m_1m_2}{m_1 + m_2}; \quad . \quad (2)$$

but  $n_1m_1 = \rho_1$ , the density of the first gas, and

$$p_1 = n_1m_1\kappa_1^2/2 = \rho_1\kappa_1^2/2, \text{ so that (1) becomes}$$

$$\rho_1\alpha_1 = \frac{d\rho_1}{dx} \frac{3}{8} \frac{\kappa_1^2}{(\kappa_1^2 + \kappa_2^2)^{\frac{1}{2}}} \frac{m_1 + m_2}{m_2} \frac{1}{\pi^{\frac{1}{2}}(a_1 + a_2)^2(n_1 + n_2)}. \quad . \quad (3)$$

The coefficient of  $d\rho_1/dx$  is by definition the coefficient of diffusion  $D$  ; remembering that  $\kappa_1^2/\kappa_2^2 = m_2/m_1$ , we get

$$D = \frac{3}{8} \kappa_1 \left( \frac{m_1 + m_2}{m_2} \right)^{\frac{1}{2}} \frac{1}{\pi^{\frac{1}{2}}(a_1 + a_2)^2(n_1 + n_2)}. \quad . \quad . \quad (4)$$

Meyer's method of proceeding is quite different. He says that as the density of one of the diffusing gases diminishes in one direction, then, if a plane is drawn anywhere at right angles to this direction, the density increases on one side and diminishes on the other, so that more molecules cross the

plane from the side of increasing density than from that of decreasing density, and diffusion results. Thus if  $n_1$  is the number of molecules per unit volume at the plane, that at a small distance  $x$  from it will be  $n_1 + x dn_1/dx$ . The number of molecules leaving an element  $dx$  after encounter in it to cross the plane before the next encounter must be proportional to  $n_1 + x dn_1/dx$ , to  $dx$ , to the mean number of collisions per second  $v_1/\lambda_1$ , where  $\lambda_1$  is the mean free path of the molecules of the first set near  $x$ , and finally to  $e^{-x/\lambda_1}$  the probability of a path greater than  $x$ , so that the number of molecules of the first set which cross the plane from one side in unit time is proportional to

$$\int_0^{\infty} \bar{v}_1 (n_1 + x dn_1/dx) e^{-x/\lambda_1} dx / \lambda_1$$

(although  $x$  was stipulated to be small to justify the expression  $n_1 + x dn_1/dx$ , no harm can come of integrating to  $\infty$ , because the value of the integral becomes negligible for all values of  $x$  greater than a few times  $\lambda_1$ ). The number of molecules crossing from the other side is proportional to

$$\int_0^{\infty} \bar{v}_1 (n_1 - x dn_1/dx) e^{-x/\lambda_1} dx / \lambda_1,$$

so that the excess accumulating in unit time on one side is proportional to

$$2\bar{v}_1 \int_0^{\infty} x e^{-x/\lambda_1} dx dn_1/dx \lambda_1,$$

that is to  $2\bar{v}_1 \lambda_1 dn_1/dx$ . The number of molecules of the other set crossing in the opposite direction is proportional to  $2\bar{v}_2 \lambda_2 dn_2/dx$ . As these two expressions are not equal, there is a gain of molecules on one side of the plane and a loss on the other proportional to

$$2(\bar{v}_1 \lambda_1 dn_1/dx - \bar{v}_2 \lambda_2 dn_2/dx);$$

and to preserve the uniformity of pressure Meyer supposes a bodily motion of the mixed gases to take place so as to carry this number of molecules in the opposite direction, of which the fraction  $n_1/(n_1 + n_2)$  belongs to the first set and  $n_2/(n_1 + n_2)$  to the second: thus the diffusion-stream of the first gas is proportional to

$$2\bar{v}_1 \lambda_1 \frac{dn_1}{dx} - \frac{2n_1}{n_1 + n_2} \left( \bar{v}_1 \lambda_1 \frac{dn_1}{dx} - \bar{v}_2 \lambda_2 \frac{dn_2}{dx} \right),$$

that of the other being equal and opposite. On account of the uniformity of pressure,  $dn_1/dx = dn_2/dx$  and the diffusion-



stream is proportional to

$$2 \frac{dn_1}{dx} \frac{n_2 \bar{v}_1 \lambda_1 + n_1 \bar{v}_2 \lambda_2}{n_1 + n_2},$$

and the diffusion-coefficient to

$$(n_2 \bar{v}_1 \lambda_1 + n_1 \bar{v}_2 \lambda_2) / (n_1 + n_2).$$

The defect of Meyer's theory is that it takes no account of the actually existing diffusion velocities in the two sets. Supposing the process of diffusion to be arrested suddenly by some cause which then suddenly ceases to act, Meyer's method shows how the diffusion-streams would begin to flow again, but it cannot follow the process after that, because it takes no cognizance of the bodily motions existing in the two sets.

Tait's theory takes account of both Stefan's and Meyer's causes; he supposes the molecules of each medium besides their velocities of agitation to have velocities of translation *en masse*  $\alpha_1$  and  $\alpha_2$ , and then calculates the quantities of each flowing in unit time across unit section, these quantities depending on  $\alpha_1$  and  $\alpha_2$  and on expressions similar to Meyer's. The velocities  $\alpha_1$  and  $\alpha_2$  are determined exactly as in Stefan's method, so that Tait's method labours under this difficulty, that he supposes each molecule of each set to have a certain velocity combined with the velocity of agitation, and yet this velocity is different from that of the set as a whole.

On theoretical grounds, therefore, Stefan's theory appears not to have been improved by the later attempts, and, further, it seems to me not to have been sufficiently recognized that Stefan has given satisfactory experimental proof of the soundness of his method of treating the diffusion problem; for exactly on the lines of his theory of the diffusion of two gases into one another he constructed a theory of the evaporation of a liquid into a gas, which led to a striking formula for the velocity of evaporation of a liquid, a formula verified by his own and Winkelmann's experiments. As Stefan's elegant theory of evaporation will only take a few lines to reproduce here, and as it gives a valuable method of determining diffusion-coefficients, it may as well be reproduced in the present connexion.

Suppose a tube half filled with a liquid whose properties are to be denoted by suffix 1 evaporating into an atmosphere with suffix 2, but with fresh liquid added from below so as always to keep the free surface of the liquid at a fixed mark on the tube; then, when a stationary state is established, there is a steady diffusion-stream of the vapour through the upper

half of the tube while the gas in the tube is at rest. Thus, in Stefan's theory of diffusion already given, we have only to put  $\alpha_2=0$  and we can proceed at once to calculate the velocity of evaporation in terms of the coefficient of diffusion. In the expression (2) for  $R$ ,  $\alpha_1(1+n_1/n_2)$  stands for  $\alpha_1+\alpha_2$ , so that if  $\alpha_2=0$  the term  $n_1/n_2$  in  $R$  drops out, and the equations (3) and (4), which can be written  $\rho_1\alpha_1=Dd\rho_1/dx$ , will in the case of evaporation have to be written

$$\rho_1\alpha_1=D\frac{d\rho_1}{dx}\frac{n_1+n_2}{n_2}.$$

Let  $p_1$  and  $p_2$  be the partial pressures of vapour and gas, and  $p$  the total pressure  $p_1+p_2$  at which the evaporation is going on, then  $(n_1+n_2)/n_2=p/p_2$ ; and if  $\rho$  is the density of the vapour under some standard pressure  $P$ , then  $\rho_1$  can be taken as equal to  $\rho p_1/P$  if the departure from Boyle's law is not too great, and then the last equation becomes

$$\rho_1\alpha_1=\frac{D\rho p}{Pp_2}\frac{dp_1}{dx}=\frac{D\rho p}{P(p-p_1)}\frac{dp_1}{dx}=D\rho\frac{p}{P}\frac{d\log(p-p_1)}{dx};$$

but  $\rho_1\alpha_1$  is the mass of vapour that crosses each unit section of the tube in unit time, and in the steady state is constant: therefore  $d\log(p-p_1)/dx$  is constant. Let  $h$  be the distance of the liquid surface below the open end of the tube, where  $p_1$  is 0 while at the liquid surface it is  $p_s$ , the saturation-pressure of the liquid at the temperature of the experiment, then

$$d\log(p-p_1)/dx=\frac{\log p-\log(p-p_s)}{h},$$

and the law of evaporation for a liquid whose surface is kept at distance  $h$  below the open end of a tube is

$$\rho_1\alpha_1=\frac{D\rho p}{Ph}\log\frac{p}{p-p_s}.$$

If the level of the liquid is not kept constant in the tube, but is allowed to fall as the liquid evaporates, then, as  $\rho_1\alpha_1$  is the mass which evaporates in unit time, if  $\sigma$  is the density of the liquid and  $dh/dt$  the velocity with which the surface of the liquid falls,  $\rho_1\alpha_1=\sigma dh/dt$ , and then

$$\left. \begin{aligned} h dh &= D \frac{\rho p}{\sigma P} dt \log \frac{p}{p-p_s}, \\ \frac{1}{2}(h_1^2 - h_0^2) &= (t_1 - t_0) D \frac{\rho p}{\sigma P} \log \frac{p}{p-p_s} \end{aligned} \right\} \dots \dots \dots (5)$$

This is Stefan's expression (*Sitz. Akad. Wien*, lxviii. 1873).

In the case where the level of the liquid is allowed to fall the velocity of the gas is not exactly 0, and in a later paper (*Sitz. Akad. Wien*, xcvi. 1890) Stefan has given a calculation wherein the small value of  $\alpha_2$  is taken account of. By very simple experiments on the evaporation of ethyl oxide and carbon disulphide in test-tubes, Stefan verified his expression first as regards the relation of  $h$  and  $t$  at constant temperature, that is at constant  $p_s$ , and then as regards the very characteristic factor  $\log p/(p-p_s)$  in which the saturation-pressure enters, by studying the evaporation of ethyl oxide at temperatures ranging from  $11^\circ.3$  C. to  $28^\circ.7$ , where the range in the saturation-pressure  $p_s$  is from 302 millim. of mercury to 605.

Winkelmann has still more thoroughly verified Stefan's evaporation theory in applying it in an extended series of experiments to the determination of the diffusion-coefficients of a number of vapours into air, hydrogen, and carbon dioxide (*Wied. Ann.* xxii., xxiii., xxxiii., xxxvi.). As regards the formula (5) the most important part of Winkelmann's work is his further verification of the soundness of the factor  $\log p/(p-p_s)$  by varying  $p$  in the case of water from 61 millim. to 749, while  $p_s$  was about 1.5 millim.

The correctness of Stefan's formula (4) for the diffusion of gases composed of forceless molecules seems to me therefore to be well assured by the successful application of the principles involved in it to the details of the process of evaporation; and the foregoing brief sketch of his theory serves as the most natural introduction to a theory of gaseous diffusion wherein the attractions of molecules are taken account of.

Let us first see wherein the expression

$$D = \left( \frac{m_1 + m_2}{m_2} \right)^{\frac{1}{2}} \frac{3\kappa_1}{8\pi^{\frac{1}{2}}(a_1 + a_2)^2(n_1 + n_2)}$$

for the diffusion-coefficient of forceless molecules applies to natural gases and wherein it fails to apply. As  $m_1\kappa_1^2$  is proportional to absolute temperature  $T$ , and  $n_1 + n_2$  is proportional to  $p/T$ , where  $p$  is the pressure at which the diffusion goes on,

$$D \propto \frac{T^{\frac{3}{2}}}{p} \left( \frac{1}{m_1} + \frac{1}{m_2} \right)^{\frac{1}{2}} \frac{1}{(a_1 + a_2)^2} \dots \dots (6)$$

Thus the theoretical diffusion-coefficient varies inversely as the pressure, which has been proved experimentally by Loschmidt to be the case for the natural gases (*Sitz. Akad.*

*Wien* lxii. 1871). The theoretical coefficient also varies as the  $3/2$  power of the absolute temperature, but it has been shown by Loschmidt and Obermayer (*Sitz. Akad. Wien*, lxi., lxii., lxxv., lxxxi., lxxxv., lxxxvii., xcvi.), in experiments on several pairs of gases, that their coefficients of diffusion vary more rapidly with temperature than according to the theoretical law. They found empirically that the coefficients vary as powers of the temperature, ranging from 1.75 to 2 instead of the 1.5 of the theory of forceless molecules. Here is where the effect of molecular force comes in, just as in the case of viscosity.

In connexion with viscosity it was shown that with like molecules the effect of molecular force on the number of collisions of spherical molecules of radius  $a$  is to make it the same as for forceless molecules in which  $(2a)^2$  is increased to  $(2a)^2\{1 + 2mf(1/2a)/\bar{V}^2\}$ , where  $m^2f(1/2a)$  is the potential energy of two molecules in contact, and  $\bar{V}^2$  is the mean square of the relative velocity. So for unlike molecules of masses  $m_1$  and  $m_2$  and radii  $a_1$  and  $a_2$ , with potential energy  $m_1m_2f(1/a_1 + a_2)$  at contact and mean relative squared velocity  $\bar{V}^2$ , the effect of molecular force on the number of collisions is to make it the same as for a pair of forceless spheres with  $(a_1 + a_2)^2$  enlarged in the ratio

$$\{1 + (m_1 + m_2)f(1/a_1 + a_2)/\bar{V}^2\}.$$

Now  $v_1^2$  and  $v_2^2$  denoting the mean squared velocities of  $m_1$  and  $m_2$ ,

$$\bar{V}^2 = \overline{v_1^2} + \overline{v_2^2} = \frac{3}{2}(\kappa_1^2 + \kappa_2^2),$$

and  $\kappa_1^2 + \kappa_2^2 = \kappa_1^2(1 + \kappa_2^2/\kappa_1^2) = \kappa_1^2(1 + m_1/m_2),$

so that the ratio becomes

$$1 + m_1m_2f(1/a_1 + a_2)/\frac{3}{2}m_1\kappa_1^2,$$

or  $1 + m_1m_2f(1/a_1 + a_2)/m_1v_1^2,$

which may be written  $1 + {}_1C_2/T,$

and then the expression for the diffusion-coefficient of attracting molecules derived from (6) for forceless molecules is

$$D \propto \frac{T^{\frac{3}{2}}}{p} \left( \frac{1}{m_1} + \frac{1}{m_2} \right)^{\frac{1}{2}} \frac{1}{(a_1 + a_2)^2(1 + {}_1C_2/T)} \cdot \cdot \cdot \quad (7)$$

As the diffusion-coefficients are all referred to a pressure of one atmosphere, we have for the ratio of  $D_2$  at  $T_2$  to  $D_1$  at  $T_1$ ,

$$\frac{D_2}{D_1} = \left( \frac{T_2}{T_1} \right)^{\frac{3}{2}} \frac{1 + {}_1C_2/T_1}{1 + {}_1C_2/T_2} \cdot \cdot \cdot \cdot \cdot \quad (8)$$

The experimental determinations for any one pair of gases are not numerous enough, or at widely enough separated temperatures, to test this theoretical relation between  $D$  and  $T$ , but as the corresponding relation in viscosity has been verified experimentally over a temperature range of 1400 degrees, it is not necessary to have such verification here before proceeding. From a single determination of the ratio of  $D_2$  to  $D_1$  at any two temperatures  $T_2$  and  $T_1$  we can calculate from (8) a value of  ${}_1C_2$  which is a measure of the potential energy of molecules 1 and 2 in contact. Loschmidt was the first to measure diffusion-coefficients at one, or at different temperatures, but as von Obermayer's results are later and more elaborately determined it will suffice to use them. He has measured the diffusion-coefficients of six pairs of gases at ordinary temperatures, and at  $61^{\circ}5$  C. (*Sitz. Akad. Wien*, lxxx.), namely, those of carbon dioxide with air, hydrogen, and nitrogen monoxide  $N_2O$ , and those of oxygen with hydrogen, nitrogen, and carbonic oxide. In the following table are given for each pair of gases the two temperatures of v. Obermayer's experiments, the values of the diffusion-coefficients at these temperatures, and the values of  ${}_1C_2$  for each pair calculated therefrom. The diffusion-coefficients are given in terms of the centimetre and second as units, and are the volumes of the gases in cub. centim. measured at the temperature of the experiment and at a pressure of 1 atmosphere which pass in one second in a diffusion-stream where the fall of the partial pressure of each gas is 1 atmosphere in 1 centimetre :—

Pair of Gases.	T.	D.	${}_1C_2$ .
CO <sub>2</sub> and Air.....	281	·143	250
	334·5	·201	
CO <sub>2</sub> and H <sub>2</sub> .....	284	·580	106
	334·5	·773	
CO <sub>2</sub> and N <sub>2</sub> O .....	284	·0996	380
	334·5	·1394	
O <sub>2</sub> and H <sub>2</sub> .....	286	·736	100
	334·5	·967	
O <sub>2</sub> and N <sub>2</sub> .....	286	·193	136
	334·5	·256	
O <sub>2</sub> and CO .....	273	·187	124
	334·5	·269	

If the law of force is that of the inverse fourth power, or

the law of energy is that of the inverse cube, then

$$m_1 m_2 f(1/\overline{a_1 + a_2}) = m_1 m_2 {}_1A_2/(a_1 + a_2)^3,$$

and if we know relative values of  $a_1$  and  $a_2$ , then  ${}_1C_2(a_1 + a_2)^3$  will give relative values of  ${}_1A_2 m_1 m_2$ .

There are two sources of relative values of the molecular radii  $a_1$  and  $a_2$ :—first, the viscosity of the separate gases, and in my paper on the Viscosity of Gases and Molecular Force relative values of  $(2a_1)^2$  are given as  $(2a)^2$  (relative); the second source is values of  $\beta$  the limiting volume of a gramme of a substance as obtained from its characteristic equation as a liquid, and given for various substances in the papers on the “Laws of Molecular Force” (Phil. Mag., March 1893) and the “Viscosity of Gases and Molecular Force” (Phil. Mag., Dec. 1893): if  $M$  is the ordinary chemical molecular mass (weight) of the substance, then  $M\beta$  is proportional to  $(2a)^3$  and  $(M\beta)^{\frac{1}{3}}$  may be taken as giving a relative value of  $2a$ , and then  $a_1 + a_2$  is given by  $(M_1\beta_1)^{\frac{1}{3}}/2 + (M_2\beta_2)^{\frac{1}{3}}/2$ .

The latter source of values of  $a$  is preferable at present, as it yields values for more substances than the former. For the gases of v. Obermayer’s experiments we have the following values:—

	H <sub>2</sub> .	O <sub>2</sub> .	N <sub>2</sub> .	CO <sub>2</sub> .	N <sub>2</sub> O.
$\beta$ .....	4.3	604	81	69	66
$M$ .....	2	32	28	44	44
$(M\beta)^{\frac{1}{3}}/2$ ...	1.025	1.34	1.415	1.56	1.535

There is no direct determination of  $\beta$  for CO, but from the molecular domains (volumes) of a number of carbon compounds I have deduced 1.35 as an approximate value of  $(M\beta)^{\frac{1}{3}}/2$  for CO. With the above values we get for

$$10^{-1}{}_1C_2\{(M_1\beta_1)^{\frac{1}{3}}/2 + (M_2\beta_2)^{\frac{1}{3}}/2\}^3$$

the following values, which are relative values of  ${}_1A_2 m_1 m_2$ ; air will be treated as pure N<sub>2</sub>:—

CO <sub>2</sub> & N <sub>2</sub> .	CO <sub>2</sub> & H <sub>2</sub> .	CO <sub>2</sub> & N <sub>2</sub> O.	O <sub>2</sub> & H <sub>2</sub> .	O <sub>2</sub> & N <sub>2</sub> .	O <sub>2</sub> & CO.
656	182	1122	131	282	241

It should be noticed that these numbers show a large range of value, namely, from 131 to 1122. Now in the paper on the Viscosity of Gases and Molecular Force relative values are given for  ${}_1A_1 m_1^2$  or  $Am^2$ , the corresponding factor in the expression for the attraction between like molecules; they are given as  $10^{-1}M\beta C$ , which in the notation of this paper would be

$$10^{-1}{}_1C_1\{(M_1\beta_1)^{\frac{1}{3}}/2 + (M_1\beta_1)^{\frac{1}{3}}/2\}^3,$$

and are now reproduced for the substances of v. Obermayer’s experiments with the addition of an approximate value for CO:

H <sub>2</sub> .	N <sub>2</sub> .	O <sub>2</sub> .	CO <sub>2</sub> .	N <sub>2</sub> O.	CO.
46[68]	247	245	839	755	198

The value 68 for H<sub>2</sub> is the experimental one, which is very uncertain; the value 46 would bring H<sub>2</sub> into accord with all other bodies, as may be seen in the "Viscosity of Gases and Molecular Force."

The most natural relation to expect between  ${}_1A_1m_1^2$ ,  ${}_2A_2m_2^2$ , and  ${}_1A_2m_1m_2$  is  ${}_1A_2m_1m_2 = ({}_1A_1m_1^2 {}_2A_2m_2^2)^{\frac{1}{2}}$ , and accordingly we now give values of  $10^{-1}(M_1\beta_{11}C_1M_2\beta_{22}C_2)^{\frac{1}{2}}$ , obtained from the numbers just given, and the ratio of

$$10^{-1}C_2\{(M_1\beta_{11})^{\frac{1}{2}}/2 + (M_2\beta_{22})^{\frac{1}{2}}/2\}^3 \text{ given above to } 10^{-1}(M_1\beta_{11}C_1M_2\beta_{22}C_2)^{\frac{1}{2}}.$$

	CO <sub>2</sub> & N <sub>2</sub> .	CO <sub>2</sub> & H <sub>2</sub> .	CO <sub>2</sub> & N <sub>2</sub> O.
$10^{-1}(M_1\beta_{11}C_1M_2\beta_{22}C_2)^{\frac{1}{2}}$ .....	455	196	796
Ratio.....	1.4	.92	1.4
	O <sub>2</sub> & H <sub>2</sub> .	O <sub>2</sub> & N <sub>2</sub> .	O <sub>2</sub> & CO.
$10^{-1}(M_1\beta_{11}C_1M_2\beta_{22}C_2)^{\frac{1}{2}}$ .....	106	246	220
Ratio.....	1.2	1.16	1.1

The mean value of the ratio is 1.2, and the departures of some of the individual numbers from the mean, though large, are not larger than could be caused by only slight error in the experiments or the theory, for it must be remembered that the constants  ${}_1C_2$  occur in equation (8) in such a manner as to make their values when calculated from that equation very sensitive to small errors in the ratio of the diffusion-coefficients at two temperatures. Thus, notwithstanding the high degree of accuracy attained by v. Obermayer in his elaborate experiments, it must be allowed that the last series of numbers is as nearly constant as can be expected. To show this clearly it will be best to assume that the ratio is 1, and calculate  ${}_1C_2$  from the equation

$${}_1C_2\{(M_1\beta_{11})^{\frac{1}{2}}/2 + (M_2\beta_{22})^{\frac{1}{2}}/2\}^3 = (M_1\beta_{11}C_1M_2\beta_{22}C_2)^{\frac{1}{2}}, \quad (9)$$

and then by the equation (8) calculate values of the ratio of the diffusion-coefficients at v. Obermayer's two temperatures for comparison with his experimental values:—

	CO <sub>2</sub> & N <sub>2</sub> .	CO <sub>2</sub> & H <sub>2</sub> .	CO <sub>2</sub> & N <sub>2</sub> O.	O <sub>2</sub> & H <sub>2</sub> .	O <sub>2</sub> & N <sub>2</sub> .	O <sub>2</sub> & CO.
Exper. ...	1.41	1.33	1.40	1.31	1.32	1.43
Theory...	1.38	1.34	1.38	1.31	1.32	1.43

The largest discrepancy between theory and experiment amounts to 2 per cent., and it cannot be claimed that the ratio of the diffusion-coefficients at two temperatures, as measured experimentally, can be guaranteed correct to within 2 per cent., especially as the experimental measurements only

yield values of the diffusion-coefficients by the intervention of quite an elaborate theory of the experiment.

The outcome of the investigation so far, then, is that v. Obermayer's experiments (in continuation of Loschmidt's) on the temperature variation of diffusion establish at least the approximate truth of the law that the parameter  ${}_1A_2m_1m_2$  in the attraction of two unlike molecules of masses  $m_1$  and  $m_2$  is equal to the square root of the product of the parameters  ${}_1A_1m_1^2$  and  ${}_2A_2m_2^2$  for the like molecules. To test the truth of the law in an independent manner, some experiments have been carried out on the surface-tension of mixed liquids and will be described in another paper.

Meanwhile there is interesting matter to discuss in connexion with diffusion. It can be seen how desirable are experiments on the temperature variation of the diffusion-coefficients of many more pairs of gases. This variation could be prophesied for a large number of pairs of gases by calculating  ${}_1C_2$  according to equation (9), using therein the values of  $\beta$  and  ${}_1C_1$  given in the paper on the Viscosity of Gases and Molecular Force, but the calculations would possess more interest if carried out in connexion with the experiments than at present. However, as the diffusion-coefficients of many more pairs of gases have already been determined experimentally at one temperature, it seems at first sight to be possible to determine the corresponding values of  ${}_1C_2$  from them in the following manner. Let us write our relation (7) in the form

$$D = BT^{\frac{3}{2}} \frac{(1/M_1 + 1/M_2)^{\frac{1}{2}}}{\{ (M_1\beta_1)^{\frac{1}{2}}/2 + (M_2\beta_2)^{\frac{1}{2}}/2 \}^2 (1 + {}_1C_2/T)}, \quad \dots \quad (10)$$

where B is a constant the same for all pairs, then for the six pairs of gases already studied, as we know all the variables, we can obtain values of B which ought to be all nearly the same. But when the calculation is made, using the lower value of T in each of v. Obermayer's experiments, which is about 284, it is found that B, instead of being constant, is closely proportional to  $1 + {}_1C_2/T$ , as the following values show:—

	CO <sub>2</sub> & N <sub>2</sub> .	CO <sub>2</sub> & H <sub>2</sub> .	CO <sub>2</sub> & N <sub>2</sub> O.	O <sub>2</sub> & H <sub>2</sub> .	O <sub>2</sub> & N <sub>2</sub> .	O <sub>2</sub> & CO.
10 <sup>3</sup> B .....	2·09	1·53	2·19	1·58	1·73	1·69
10 <sup>3</sup> B/(1 + ${}_1C_2/T$ )..	1·11	1·12	·94	1·17	1·17	1·16

This curious result has some interesting bearings. In the first place, it means that the diffusion-coefficients of actual gases at temperatures about 284 absolute are related to one another almost as they would be if the molecules were forceless spheres, and this explains why the investigators of



diffusion have hitherto found fair agreement between the results of experiment at ordinary temperatures and the kinetic theory of forceless perfectly restitutional spherical molecules. The immediate effect of the result on our present inquiry is to render illusory the hope of obtaining values of  $\frac{1}{2}C_2$  for the various pairs of gases for which Loschmidt and v. Obermayer have found values of the diffusion-coefficient at only one temperature near 284, for as regards these values we have just seen that the molecules behave almost as if forceless. It may be suggested that the failure of  $B$  to prove constant is due to inadequacy of Stefan's theory of diffusion, but the expressions for the diffusion-coefficient given by Meyer and Tait gave on trial about the same results as Stefan's; so that the failure of  $B$  to prove constant is not due to any peculiarity of Stefan's theory. We have to go deeper for the reason, and in doing so have to open up a very important department of molecular dynamics of which at present we know but little, namely, the nature of collisions between molecules. Hitherto in the kinetic theory it has been assumed that the forces called into play during the collision of two molecules are such as they would be if the molecules were perfectly restitutional spheres, and the assumption seems to have worked well as regards the general phenomena of gases; but in reality it was not required there, and could be replaced by the assumption that the translatory kinetic energy of a number of molecules is a constant fraction of their total kinetic energy. The usual assumption of perfect restitutionality causes no difficulty in connexion with the theory of the viscosity of a single gas, because the nature of the collisional forces between molecules is not directly involved in that theory; but in the theory of diffusion, as well as in that of the characteristic equation of the element gases, the forces involved in collision enter as an essential element of the calculation. Now in the paper on the Viscosity of Gases and Molecular Force, in connexion with the theory of the characteristic equation of the element gases, just such a discrepancy as we have encountered in diffusion cropped up between the behaviour of actual gases and the theory of a medium composed of attracting perfectly restitutional spheres; and it was pointed out that in some way, which at present must be called accidental, the departure from perfect restitutionality in the collisions compensated for a certain effect of molecular attraction in such a way as to make the molecules behave in one respect as if they were forceless. It seems desirable, therefore, to bring out clearly the parallelism of the two cases.

In the theoretical characteristic equation of a medium

made of attracting smooth perfectly restitutional spheres, one term is the virial of the collisional forces of all the spheres in unit mass which takes the form  $\Sigma a\mu\nu/2$  (see Viscosity of Gases and Molecular Force), where  $a$  is the radius of a sphere,  $\mu$  the average momentum imparted to a sphere in a collision, and  $\nu$  the average number of collisions per sphere per second, the summation to extend to all spheres in unit mass. This is closely similar to the expression which comes in in diffusion for the resistance experienced by one medium in passing through another, and which was written  $\mu\nu$ . In the virial expression  $\mu$  is momentum due to velocity of agitation, while in the diffusion resistance  $\mu$  is the momentum due to relative motion of the two media, which is very slow compared to the velocities of agitation. In the diffusion resistance  $\nu$  denotes the number of collisions per second of a sphere of one set with the spheres of the other in unit volume. It was shown that  $\Sigma a\mu\nu/2$  when evaluated takes the form

$$\frac{3}{2}RT \frac{b}{v-b} (1 + {}_1C_1/T)^{\frac{3}{2}};$$

so that the theoretical characteristic equation becomes

$$pv = RT \left\{ 1 + \frac{b}{v-b} (1 + {}_1C_1/T)^{\frac{3}{2}} \right\} - \frac{a}{v};$$

whereas Amagat's experiments on  $H_2$ ,  $O_2$ ,  $N_2$ , and  $CH_4$  above the critical volume can be represented by the form

$$pv = RT \left\{ 1 + \frac{b}{v-b} \right\} - \frac{a}{v};$$

so that the factor  $(1 + {}_1C_1/T)^{\frac{3}{2}}$  due to molecular force seems to fall out. Now in the diffusion expression it is a factor approximately equal to  $1 + {}_1C_2/T$  that appears to drop out; and the main difference between the two cases is that in diffusion the velocity of diffusion involved in the momentum is small compared to the average velocity of agitation involved in the  $\mu$  of the collisional virial. Thus it appears that the momentum communicated from molecule to molecule in a collision is not transmitted in the same manner as with smooth perfectly restitutional attracting spheres, but that there is some mechanism by which the transmission is made to depend on the ratio of the potential energy at contact to the mean kinetic energy in such a manner as to make the final effect of the forces acting during the collision of molecules the same as if the molecules were both forceless and perfectly restitutional smooth spheres. The mechanism is probably that which preserves proportionality between the mean translatory kinetic energy and the mean vibratory energy of a molecule;

and the difference between the diffusion case and that of the collisional virial may perhaps lie in the fact that the mechanism does not operate in the same manner as regards the mass motion of diffusion and the molecular motion of heat. But the whole question of molecular collision is so large a one that it will require considerable research to itself; from the glimpse we have got into it, it appears that the momentum imparted to a molecule during a collision, instead of being  $\mu$  as calculated on the assumption that the molecules are smooth perfectly restitutional spheres, is  $h\mu$ , where  $h$  is a parameter characteristic of the pair of molecules colliding, and which we have found empirically in the case of diffusion to be approximately proportional to  $1 + \frac{1}{2}C_2/T$ . It may be worth while noting a certain regularity in the departure from strict proportionality, or in the departure of  $10^3B/(1 + \frac{1}{2}C_2/T)$  from constancy: for the two triatomic molecules  $\text{CO}_2$  and  $\text{N}_2\text{O}$  its value is least, namely, .94; for the triatomic  $\text{CO}_2$  with diatomic  $\text{N}_2$  and  $\text{H}_2$  it is 1.11 and 1.12; while for the three diatomic pairs  $\text{O}_2$  with  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{CO}$ , it is 1.17, 1.17, and 1.16.

With Loschmidt's and v. Obermayer's diffusion-coefficients for a number of pairs of gases at about  $15^\circ \text{C}$ ., we can test more extensively our empirical relation that at about that temperature the diffusion-coefficient is proportional to

$$(1/M_1 + 1/M_2)^{\frac{1}{2}} / \{ (M_1\beta_1)^{\frac{1}{2}}/2 + (M_2\beta_2)^{\frac{1}{2}}/2 \}^2.$$

The data are available for sixteen pairs including the six already considered, and as the experimenters have reduced their results to values at  $0^\circ \text{C}$ . by the approximate formula

$$D_{273}/D_T = (273/T)^2,$$

which is near enough to the truth for small differences between  $T$  and  $273$ , we will take the values  $D_{273}$  as suitable for our present purpose. The additional values required for  $(M\beta^{\frac{1}{2}})/2$  are:—

	$\text{CH}_4$ .	$\text{C}_2\text{H}_4$ .	$\text{C}_2\text{H}_6$ .	$\text{SO}_2$ .
$\beta$ .....	1.59	1.53	1.4 (near)	.55
$M$ .....	16	28	30	64
$(M\beta)^{\frac{1}{2}}/2 \dots$	1.47	1.75	1.74	1.63

With these and the values already given, and the values of  $D$  reproduced from v. Obermayer and Loschmidt, the values of

$$(1/M_1 + 1/M_2)^{\frac{1}{2}} / \{ (M_1\beta_1)^{\frac{1}{2}}/2 + (M_2\beta_2)^{\frac{1}{2}}/2 \}^2 D$$

have been calculated as given along with the diffusion-coefficients in the following table :—

H <sub>2</sub> and O <sub>2</sub>	N <sub>2</sub>	CO.	CH <sub>4</sub> .	CO <sub>2</sub> .	N <sub>2</sub> O.	C <sub>2</sub> H <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .	SO <sub>2</sub> .
D <sub>273</sub> ...	·667	·645	·647	·625	·532	·532	·486	·484
	·195	·191	·199	·193	·203	·207	·194	·209
CO <sub>2</sub> and O <sub>2</sub>	N <sub>2</sub> .	N <sub>2</sub> O.	CO.	O <sub>2</sub> and N <sub>2</sub> .		CO.	CO and C <sub>2</sub> H <sub>4</sub> .	
D <sub>273</sub> ...	·136	·135	·193	·143			·178	·187
	·205	·201	·248	·199			·193	·190
								·122
								·237

The values of

$$(1/M_1 + 1/M_2)^{\frac{1}{2}} / \{ (M_1\beta_1)^{\frac{1}{2}}/2 + (M_2\beta_2)^{\frac{1}{2}}/2 \}^2 D$$

are nearly constant, though showing on the whole a tendency to increase with the number of atoms in the diffusing molecules, as we already noted in connexion with  $10^3 B/(1 + {}_1C_2/T)$  for the original six pairs of gases.

The last table can be greatly extended, thanks to the experiments carried out by Winkelmann for determining diffusion-coefficients according to Stefan's evaporation method founded on his equation marked (5) in the present paper. He has determined the rates of evaporation of a number of esters from C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> to C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>, and ethyl oxide, carbon disulphide, and benzene in air, hydrogen, and carbon dioxide at different temperatures, and has calculated the corresponding coefficients of diffusion.

In order to obtain the values of D<sub>273</sub> it is necessary to obtain approximate values of  ${}_1C_2$  for use in the equation

$$\frac{D_{273}}{D_T} = \left( \frac{273}{T} \right)^{\frac{3}{2}} \frac{1 + {}_1C_2/T}{1 + {}_1C_2/273}.$$

These can be calculated from equation (9) if we know  ${}_1C_1$  and  $M\beta$  for the esters. The values of  ${}_1C_1$  can be obtained in the following manner:—In the paper on the Viscosity of Gases and Molecular Force it is shown that for compounds

$$M\beta {}_1C_1 10^{-2} = 21M^2l/2,$$

where  $l$  is the virial constant of molecular attraction in the characteristic equation of the substance; values of  $M^2l$  for a large number of bodies being given in the Laws of Molecular Force (Phil. Mag., March 1893) along with methods of calculating them for any body. As regards  $M\beta$  for the esters, I have found by determining  $\beta$  that for C<sub>*n*</sub>H<sub>*2n*</sub>O<sub>2</sub>,

$$M\beta = 29 + 17.5(n-1)$$

approximately: thus all the data are to hand for calculating  ${}_1C_2$  for each of Winkelmann's diffusing pairs.

Values of  ${}_1C_2$ .

$H_2$ and $C_3H_6O_2$ .	$C_4H_8O_2$ .	$C_5H_{10}O_2$ .	$C_6H_{12}O_2$ .	$C_7H_{14}O_2$ .
146	145	144	144	144
Air and 235	237	241	243	245
CO and 383	389	395	401	405
$H_2$ and $C_8H_{16}O_2$ .	$C_9H_{18}O_2$ .	$(C_2H_5)_2O$ .	$CS_2$ .	$C_6H_6$ .
145	144	134	153	169
Air and 248	247	219	241	276
CO and 411	413	361	393	453

Winkelmann's determinations include a number of isomers, as, for instance, propyl formate, ethyl acetate, and methyl propionate of the composition  $C_4H_8O_2$ ; and in the diffusion-coefficients about to be given I have taken the mean of the isomers in each case, so that, for instance, the mean diffusion-coefficient of the bodies just mentioned is given as the value for  $C_4H_8O_2$ . When the broad principles have been established it will be time enough to take account of minor differences in the diffusion-coefficients of isomers. The following table contains the mean diffusion-coefficients obtained from Winkelmann's determinations at the temperatures of his experiments, and the values at  $0^\circ C$ . calculated by the last formula and the values of  ${}_1C_2$  just given.

Substance diffusing into		$H_2$ .	Air.	$CO_2$ .
	T.	D.	D.	D.
$C_3H_6O_2$ .....	319.2	.446	.112	.075
	293.4	.390	.100	.067
	273	.341	.087	.057
$C_4H_8O_2$ .....	339.8	.440	.111	.078
	319.1	.390	.100	.069
	273	.292	.074	.050
$C_5H_{10}O_2$ .....	364	.418	.112	.081
	339.8	.383	.099	.069
	273	.258	.065	.043
$C_6H_{12}O_2$ .....	369.5	.410	.106	.075
	339.7	.349	.087	.062
	273	.235	.057	.039
$C_7H_{14}O_2$ .....	371	.380	.095	.068
	273	.218	.053	.036
$C_8H_{16}O_2$ .....	371	.343	.085	.061
	273	.197	.047	.033
$C_9H_{18}O_2$ .....	371	.318	.078	.057
	273	.182	.043	.030
$(C_2H_5)_2O$ .....	292.9	.341	.089	.064
	283.4	.320	.083	.060
	273	.298	.078	.055
$CS_2$ .....	305.8	.463	.112	.079
	292.9	.425	.101	.073
	273	.371	.088	.063
$C_6H_6$ .....	318	.399	.101	.071
	292.9	.341	.088	.061
	273	.297	.076	.052

With these values of  $D$  at 273 the values of

$$(1/M_1 + 1/M_2)^{\frac{1}{2}} / \{ (M_1\beta_1)^{\frac{1}{2}}/2 + (M_2\beta_2)^{\frac{1}{2}}/2 \}^2 D$$

can now be calculated as for the gases, with the following results (treating air as  $N_2$ ):—

	$C_3H_6O_2$	$C_4H_8O_2$	$C_5H_{10}O_2$	$C_6H_{12}O_2$	$C_7H_{14}O_2$
$H_2$ .....	·23	·24	·25	·26	·26
Air .....	·22	·23	·24	·25	·25
$CO_2$ .....	·27	·27	·28	·28	·29

	$C_8H_{16}O_2$	$C_9H_{18}O_2$	$(C_2H_5)_2O$	$CS_2$	$C_6H_6$
$H_2$ .....	·27	·27	·23	·23	·24
Air .....	·26	·27	·22	·23	·23
$CO_2$ .....	·30	·31	·25	·26	·27

It will be noticed that with hydrogen and air at the lower members of the ester series and  $(C_2H_5)_2O$  and  $CS_2$ , the values are near to the ·2 which was about the mean value for the gases, but that they increase steadily as the series is ascended; so that the result for vapours joins on continuously with that for gases, but shows a decided departure from our empirical result for gases that for temperatures near  $0^\circ C$ . the diffusion-coefficients have nearly the same relative values as if the molecules were forceless. But it should be remembered that the results for vapours are all calculated on the assumption that they obey the gaseous laws, and therefore that care should be taken not to give much weight to them till it is ascertained, either theoretically or experimentally, what is the effect on the diffusion-coefficient of such departure from the gaseous laws as vapours show.

To carry the subject to the most suitable point at which to leave it at present, it seems best to take all the values of

$$(1/M_1 + 1/M_2)^{\frac{1}{2}} / \{ (M_1\beta_1)^{\frac{1}{2}}/2 + (M_2\beta_2)^{\frac{1}{2}}/2 \}^2 D_{273}$$

which have been given in this paper and divide them by the corresponding values of  $1 + {}_1C_2/273$ , using only the theoretical values of  ${}_1C_2$ , calculated according to equation (9). In this way, according to equation (10), we ought for attracting smooth perfectly restitutional spherical molecules to get the constant  $1/B273^{\frac{1}{2}}$  the same for all pairs of substances; and the amount of departure from constancy will furnish a good measure of the present degree of incompleteness of the kinetic theory of diffusion, the chief cause of incompleteness being, in my opinion, the assumption of perfect restitutionality in each individual collision.

## Values of

$$(1/M_1 + 1/M_2)^{1/2} / \{ (M_1\beta_1)^{1/2}/2 + (M_2\beta_2)^{1/2}/2 \}^2 D(1 + {}_1C_2/273) = 1/B273^{3/2}.$$

H <sub>2</sub> and	H <sub>2</sub> .	O <sub>2</sub> .	N <sub>2</sub> .	CO.	CH <sub>4</sub> .	CO <sub>2</sub> .
Air and	.....	·144	·144	·153	·133	·135
CO <sub>2</sub> and	·144	·140	.....			·123
	·135	·122	·123			
H <sub>2</sub> and	N <sub>2</sub> O.	C <sub>2</sub> H <sub>4</sub> .	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> .	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> .	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> .	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> .
Air and	·138	·131	·150	·157	·163	·166
CO <sub>2</sub> and	.....	.....	·119	·123	·127	·133
	·125	.....	·113	·110	·114	·115
H <sub>2</sub> and	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> .	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> .	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub> .	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.	CS <sub>2</sub> .	C <sub>6</sub> H <sub>6</sub> .
Air and	·167	·177	·178	·157	·150	·150
CO <sub>2</sub> and	·132	·139	·142	·123	·125	·115
	·115	·119	·123	·107	·107	·100

Winkelmann's values of the diffusion-coefficients for the vapours of water, the alcohols, and fatty acids have not been discussed in the present communication on account of the exceptional nature of these substances, but they will doubtless be of value when the time is ripe for a full discussion of the physical reasons of their exceptional behaviour.

Melbourne, January 1894.

## II. Coloured Cloudy Condensation, as Depending on the Temperature and the Dust-contents of the Air. By CARL BARUS\*.

[Plate V.]

1. **I**N the "koniscope" Mr. Aitken† has expressed the dust-contents of a given sample of air, in terms of the colour, or of the intensity of colour, or of the amount of exhaustion necessary to produce a given colour, when the cloudy condensation is produced by sudden expansion of the gas in a suitable tube, containing enough moisture to saturate the air. The importance of temperature is pointed out, but not evaluated. Mr. Aitken prefers to make the

\* I have availed myself of the permission of the Editors of this Magazine to reproduce here a condensed account of certain parts of a forthcoming Bulletin of the U.S. Weather Bureau, believing the subject to possess some general physical interest.

† Aitken, Proc. Roy. Soc. London, li. p. 425 *et seq.*, 1892. For a review of the earlier history of the subject (for which there is no space here) the reader is referred to my papers in the 'American Meteorological Journal,' ix. p. 488, 1893; x. p. 12, 1893. On reviewing my *résumé* I find that the tribute there paid to the breadth and thoroughness of Mr. Aitken's researches (many of which I have since repeated) is inadequate. I therefore feel bound to make this acknowledgment.

estimation in terms of the colour-intensity of the blue, and the apparatus is graduated by comparing it with the direct dust-counter. Based as this apparatus is on colour discriminations, it is not adapted to give more than a few steps of dust-contents, and Mr. Aitken chiefly recommends it for qualitative purposes, such, for instance, as may present themselves in sanitary work.

2. During the course of my experiments on the thermal distribution in steam-jets, I had frequent occasion to note the actuating steam-pressure at which the intense blue-violet field of my colour-tube merges into opaque, eventually to reappear (pressure increasing) as an orange-brown field of the first order. It struck me that here was a sufficiently sharp criterion for fixing a value of pressure depending in the given apparatus only on the temperature and the dust-contents of the inflowing air. In other words, for a given kind of air, and at a given temperature, there are two well-defined pressures at which colour (blue and yellow) vanishes into blackness. If the kind of air remains the same while its temperature varies, the paired values of pressure will also vary markedly, so that the margins of the opaque field may be mapped out in a diagram in which pressure is expressed in its dependence on temperature. It is the chief purpose of the present paper to show the character of this diagram, and to indicate the manner in which the positions of the loci vary, when the dust-contents of the inflowing air are also varied. Incidentally I will endeavour to ascertain the more immediate cause of the opaque field, and to see whether the water molecules may not themselves become nuclei of condensation, §§ 15, 16.

3. *Apparatus.*—Full details of the necessary apparatus is given in Pl. V. fig. 1, where the colour-tube is shown at AA, and the method of varying the temperature and dustiness of the inflowing air is shown at E, D, F. The colour-tube is identical in form with the apparatus described in an earlier paper\*. I need only call to mind here that the steam issues at the jet *j*, from a nozzle about .16 cm. in diameter, and that the tube AA is about 50 to 60 cm. long, and, in common with the air-hole C, about 5 cm. in diameter. The glass plates *g* and *a* are kept clear by moistening with a solution of caustic potash, and the mirror M reflects skylight through the tube. Mixed steam and air escape at B, and provision is made (not shown) for screening off extraneous light from *g*, the window through which the colour observations are made.

\* Barus, Amer. Meteorolog. Journal, ix. p. 488 (1893).



The two essential appurtenances are the thermometer *t*, to register the temperature of the inflowing air at C, and the open mercury manometer (not shown) by which the pressure of the steam entering the jet *j* is measured. Inasmuch as a mercury thermometer is not very quick in its indications, the air at a given temperature must be allowed to pass over the bulb of *t* for some time before the record is taken.

The steam used was generated in a copper globe about 25 cm. in diameter, and provided with a water-gauge and a steam-gauge. The vessel was heated by a large ring-burner\* and is strong enough to withstand, say, ten atmospheres, though in the present work pressures below two atmospheres fully suffice.

G and H are forms of air-filters to be described in § 14.

4. The air entering C is taken out of the atmosphere, the three influx tubes E, D, F passing through the window frame WW, and opening into the air on the outside (Smithsonian Park) as shown at *b, c, d*. Valves are inserted into each of these tubes at *e, f, h*, so that the quantity of air passing through any one of them may be regulated or even quite shut off. In the winter, when the valves are open, the air rushes through the tubes with considerable velocity, even when the jet *j* is not in action. This velocity increases with the steam-pressure actuating the jet, but can be regulated by shutting off the valves *e, f, h* partially.

The tube E is clear, and the air passing through it has the temperature of the atmosphere. The tube D discharges into E and is provided with a drum, containing a coil of thin lead pipe of about 0.6 cm. calibre. About 20 turns of pipe, each somewhat less than 5 cm. in diameter, in a drum 35 cm. long and somewhat less than 10 cm. in diameter, are more than sufficient. In cold weather steam is passed through the lead pipe. Hence by suitably regulating the valves *h* and *f* the air flowing through C may be kept at any desirable temperature; and as temperatures between 9° and 40° only are needed for the present purposes, this arrangement is quite satisfactory. In the summer time chilled brine or an expanding gas circulating through the coil will probably be serviceable.

The tube F also discharges into E, and is useful for increasing the dust-contents of the air entering C. For this purpose a little closed basket of wire gauze, attached to a stem passing through a perforated cork, is inserted into the tubulure *k*, as shown in the figure. A piece of phosphorus

\* This apparatus, used for other purposes, is shown in Bulletin U.S. Geolog. Survey, no. 54, p. 60 (1889).

is put into the basket. The dusty exhalation of a freshly cut surface of phosphorus is almost *nil* at  $0^{\circ}$  C., but increases with great rapidity when the temperature rises, § 26. At any given temperature above  $15^{\circ}$  its dust supply is nearly constant for a long period of time (hours); hence its availability in the present work, unless the weather is very cold. Fortunately cold temperatures can usually be dispensed with when artificially dusty air is examined.

It is to be noted that all the tubes E, D, F must pass out of the room. If, for instance, *b* opened into the room (which would often be desirable for the reasons just mentioned), then, if the jet is not in action or only slightly in action, cold air would pass into C and D, and out at *b* as well as at B into the room. At low steam-pressure the flow of dusty air would, therefore, necessarily be irregular. An advantage is secured by making the common tube *i* C long, so that the air may be well mixed before impinging upon the jet. At best, however, air dusted in this way is an inferior substitute for atmospheric air, and the results show much more fluctuation. Each of the valves, *h*, *f*, *e*, is provided with a suitable dial and an index. The valve *e* must be free from leaks. It is best, moreover, when atmospheric air is examined to remove the basket *k* altogether, and to close the hole with a cork. The hole through which F discharges into E need not be more than a few millimetres in diameter, and it is advisable to carry it into the axis of E by aid of a glass tube. The whole train of tubes is easily made of ordinary tinned drain-pipe and suitable elbows. To summarize: the faint phosphorescent glow visible on phosphorus in the dark is a nearly permanent dust-producer. This phosphorus-tainted air, discharged through an  $\frac{1}{8}$ -inch tube into the 2-inch tube of pure air, usually produces persistent colour-effects at ordinary temperatures. Thus the additional dilution\* is less than  $\frac{1}{100}$ .

5. A few remarks on the shortcomings of the apparatus may be made here. It is clear in the first place that the temperature of the air entering C will vary with the intensity of the jet, *i. e.* the velocity of current, even if the other adjustments remain unaltered. For the more rapidly the air passes through the drum D the less it is heated. This, however, is no serious inconvenience since temperature is measured at *t*.

\* It is best to provide the phosphorus tube with a glass stopcock in place of the symbolic valve of fig. 1. On proper adjustment brilliant colour-effects are obtained in this way for any reasonable length of time. The line is quite permanent so long as the stopcock is left untouched, but there is a change of colour whenever the degree of opening is varied.

Similarly the amount of dust introduced into the air will (probably) depend on the rate at which the current passes the basket at  $k$ . Hence at great jet intensities the air will be less dusty than for small intensities. I have found no easy way by which this discrepancy can be evaluated; and my experiments with artificially dusted air are intended rather to show the character of the dust variation than to map out precise loci, §§ 11-13. Fortunately the dust effect is so striking that there is no possibility of misinterpretation. Experiments which I made by introducing dust with jet pumps and aspirators showed few advantages. To vary the dust-contents uniformly at all jet-pressures, the mouths  $c$ ,  $d$  of the air-tubes must be introduced into a large artificially dusted room, instead of the atmosphere. But this method also presents grave difficulties. The final resort seems to be to examine the atmosphere at different times and in different places, or to construct apparatus for the rapid filtration of air, §§ 14, 15.

One serious theoretical question may be referred to here. It is necessary that at all steam-pressures the amount of air entering  $C$  should be nearly proportioned to the amount of issuing steam. No doubt this is nearly the case; for not only do the air- and steam-currents increase and decrease together, but the air is admitted *in excess* of the quantity necessary to produce condensation at the supersaturated parts of the jet, and it is to this condensation that the colour indications apply. If the valve  $e$  be closed, and the valves  $f$  and  $h$  all but closed, the pressures at which the margin of the opaque zone appears from blue increase; but the temperature registered at  $t$  also increases at even a greater relative rate, so that the apparent effect is, curiously enough, rather an excess than a deficiency of dust (§ 13).

I infer from this that in the work below the air is always admitted in quantity sufficient to produce its maximum dust effect. To test this question preliminarily, I replaced the 0.16 cm. nozzle by another 0.09 cm. in diameter, and thus (*cet. par.*) only discharging one third as much steam as the former. The new results virtually coincided with the old (§ 15); and hence, though the relations below were obtained from a given apparatus, they are probably true generally\* so

\* It will be expedient to consider the small differential effect of variations of the barometer, and the tendency of the pressure corresponding to "blue-opaque" to fall with the time of efflux, &c., in the Bulletin cited. Brass nozzles corrode in the course of time, so that it is advisable to make them of platinum. With some unpolished nozzles the "yellow-blue" asymptote may fall even as low as 20 centim. of mercury at 30° air-temperature.

long as the inflowing air exceeds a certain minimum quantity and the nozzle is of average smoothness. A full discussion of all these points will be in order when I come to measure the thermal distribution within the colour-tube, and particularly in the neighbourhood of the nozzle of the jet. I will then show to what extent each jet possesses special hydraulic properties\*. In a general way the jet may be advantageously compared with a Bunsen flame. For just as in the one case the blue cone is a locus indicating the speed of chemical action†, under the given conditions of mixture and efflux, so in the steam-jet the transparent cone of vapour indicates the rate at which condensation takes place. Given the rate of efflux of steam, a photographic method may then be easily devised for expressing the speed of condensation‡ numerically.

The fact that pin-hole jets are quite sufficient makes the practical construction of the apparatus (Plate V. fig. 1) on a small scale an easy possibility. A globular copper boiler, 5 inches in diameter, and a sensitive steam-gauge with a capacity of less than 15 pounds, are available for generating the steam and recording pressure.

6. *Results. Normal Atmosphere.*—The results in hand are necessarily in very great number, for the case is one in which the observer has to construct the mean value or path, when the observations themselves are unavoidably discrepant. It will therefore be expedient to avoid cumbersome tables, by expressing all the data graphically. An ulterior advantage is gained in this way, inasmuch as the broad features of the phenomena are at once evident to the eye.

In the chart, Plate V. fig. 2 (and in all succeeding charts), the abscissas indicate the temperature, in degrees C., of the air entering the colour-tube at C (fig. 1); or, in other words, the registry of the thermometer *t*. The ordinates show the pressures in centims. of mercury under which the steam is forced out of the jet. The points of the curve between 0 and about 40 cm. then show the corresponding values of air-temperature and steam-pressure, at which the blue-violet (first order) field seen in the colour-tube merges into opaque. The points of the curve lying quite above 40 cm. show the conditions at which the brown-yellows of the first order just emerge from the opaque. Curves indicating the approximate loci are drawn through the points.

\* Agreeing with the results of Aitken, *l. c.*

† Cf. W. Michelson, *Wied. Ann.* xxxvii. p. 1 (1889).

‡ A discussion of this method of investigation is given in the Bulletin.

Below about  $9^{\circ}$  C., therefore, the field is opaque at all pressures ; above  $9^{\circ}$ , the pressure at which blue changes into opaque rapidly increases with increasing temperature ; and the pressure at which brown-yellow changes to opaque decreases from an enormous value, and at even a more rapid rate as temperature increases. Both loci, curving at a gradually retarded rate, eventually reach a common asymptote at about 41 cm. (temperature being indefinitely high). At the same time the colours which were very intense at the lower temperature gradually become fainter, and the opaque zone more translucent, until at about  $40^{\circ}$  of air-temperature (depending on the size of the nozzle, § 15) the field is clear and without colour. The escaping steam is gaseous, and not visibly condensed. When temperature decreases again from  $40^{\circ}$ , white-yellow is the first colour to appear, showing that the particles here must be the smallest of the whole series. At  $35^{\circ}$  the change from faint yellowish tones to faint white-blues, when pressure is made to vary suitably (see chart) from larger to smaller values, is quite marked. There is no opaque demarcation, however, but rather a mixture of colours, for the opaque field is hardly impervious to light above  $30^{\circ}$ . Indeed one often notices a brownish field surrounding the jet, on a violet-bluish ground.

For all temperatures and pressures lying to the left of the two curves the field is opaque, and it sends off a kind of cusp to penetrate into higher temperatures. There is a characteristic difference between the contours of the two margins ; for whereas yellow-opaque after a sharp inflexion shoots up almost vertically, blue-opaque shows a regular change of curvature throughout.

At about  $13^{\circ}$  in the chart I have inscribed the approximate positions of the successive interference-colours\*, indicating their positions by a cross. This cannot be nearly so well done as the location of the opaque margin, and as the colours are of smaller interest in the present paper, I will not enter into the subject further. The contour of the successive colour-curves is easily surmised from the line for blue-opaque. Similarly above the yellow-opaque line, a family of browns, oranges, and yellows may be located.

When the dust-contents are increased, the margin of the opaque field approaches the abscissa, and hence the colour loci will be successively more crowded together.

In the chart (Plate V. fig. 2) only a single air-tube (D, fig. 1) was available. The air was heated to about  $40^{\circ}$  by the circulating steam. This was then shut off and the

\* See Barus, *Am. Met. Journ.* ix. p. 500 *et seq.*, 1893.

temperature and pressure at which the colours disappeared noted on cooling. The mercury-thermometer is scarcely sensitive enough for such observations, and the temperatures of the diagram are probably too high. I have therefore lumped all my observations between Feb. 10 and 23, 1893, in this chart, seeing that the phenomenon as a whole is well represented.

7. In the following work, however, the apparatus, Plate V. fig. 1, was used, with the phosphorus-tube closed up and the phosphorus removed. Great care was taken to wait for stationary temperatures, and about five (or more) steps between  $10^{\circ}\text{C}$ . and  $40^{\circ}\text{C}$ . were selected for observation.

The first set of experiments was made on Feb. 23, the chart\*, fig. 3, curve A being obtained in the morning, and fig. 4 in the afternoon. The day was cold, with snow covering the ground. The blue-opaque curve, A, fig. 3, virtually reproduces fig. 2; but the curve, fig. 4, differs from it inasmuch as the tangential angles in the latter case are steeper, so that the locus is less curved and rises higher than in figs. 2 or 3. In all cases yellow-opaque lies above blue-opaque. I was at first inclined to refer this to differences of the vanishing standard, believing the two curves to contain consistent observations, but differing from each other for reasons purely subjective. Whether or not this is the case can only be found by comparison with succeeding series of observations, as will presently be seen. Taking the observations at their face value, the indication is less dust for the afternoon than for the morning. The curve P found for artificially dusty air will be described below (§ 11).

8. The next series of observations were made on Feb. 27 (cloudy), 28 (rain), and on March 2 (clear). There was but little difference in the respective loci of the data except that on the latter day the asymptote was somewhat below the position for the other days (see chart, Plate V. fig. 5). The common asymptote takes a mean position (pressure,  $p=43\text{ cm.}$ ) between the corresponding values of figs. 2 and 3 ( $p=42\text{ cm.}$ ) and fig. 4 ( $p=48\text{ cm.}$ ).

9. On March 3, however, the asymptote rose again to the value  $p=46\text{ cm.}$  The weather was cloudy, antedating the storm of March 4, 1893. Two series of observations were made.

Finally, the results of March 6, 8, 10 agree in character with fig. 5; while during the intermediate date, March 7, the asymptote fell to the lower position  $p=42\text{ cm.}$  These

\* The observations FF' in fig. 3 refer to filtered air and will be described in § 14.

figures, as a whole, give some evidence in favour of an oscillation of the asymptote with the dust-contents of atmospheric air. The observed interval of oscillation is within about 8 cm. of mercury pressure, but usually much below this.

10. *General character of the Loci.*—Resuming the remarks of §6, it is seen that when the asymptotes are high, the loci as a whole show less curvature and the points between 20° and 30° C. tend to fall below the corresponding points for low asymptotes. I have endeavoured to bring the whole phenomenon into a convenient equation, in which temperature and dust-contents might appear as two variables by which the contours (pressure) of the margin of the opaque field (figs. 2 *et seq.*) are conditioned. The invention of a single form in which both the blue-opaque and the yellow-opaque margins are contained is more difficult than the fitting of a separate form for each curve, and I have not been fully successful in any case. Cumbersome equations, or such as lead to involved computations, are of little interest for the present purposes, where the object sought is merely a terse and convenient epitome of the very large number of isolated observations which go to make up each of the curves in question.

Let  $p$  be the steam-pressure actuating the jet, and  $t$  the temperature of the air into which the jet is discharged, and let  $A, B, C, n$  be constants to be presently discussed. Then

$$t = A \cdot 10^{\frac{Cp}{(p-B)^n}} \dots \dots \dots (1)$$

The quantity  $(p-B)$  in (1) is always to be taken as a numeric, *i. e.* positively; otherwise imaginary results are encountered. Suppose now this equation is tested by the data of fig. 5, as these fairly represent a mean case. Then

$p=0, t=A=9$ , by observation;

$p=B, t=\infty$ , or  $B=43$ , the height of the asymptote above the abscissa;

$p=\infty, t=\infty$ .

Hence the yellow-opaque margin, lying quite above  $p=B=43$ , corresponds directly to equation (1); whereas the blue-opaque margin, lying quite below  $p=B=43$ , corresponds to (1) with  $(p-B)$  replaced by  $(B-p)$ . Furthermore, while in the yellow-opaque branch  $p$  increases from 43 cm. to  $\infty$ ,  $t$  passes through a minimum value. It is, therefore, necessary to inquire the position and character of this uncalled for singular point. Let equation (1) be differentiated, remembering that  $t=0$  corresponds to  $p=-\infty$ , and therefore does not

enter the present problem, and that  $B=p$  has already been disposed of. Then the pressure  $p_m$ , corresponding to the minimum temperature  $t_m$  in question, is found to be

$$p_m = \frac{B}{1-n},$$

and the somewhat more involved expression of  $t_m$  is found from equation (1).

With these preliminaries, the remaining constants  $C$  and  $n$  are then easily enough, though somewhat tediously, obtained from the observations making up fig. 5, by trial. The results are as follows:—

$$A=9; C=0.013; n=0.35; B=43.$$

Steam-pressures,  $p$ , in cm. of mercury; air-temperatures,  $t$ , in degrees C.

$p = 0$ cm.	$t = 9.0^\circ$	$p = 43$ cm.	$t = +\infty^\circ$
10	9.8	44	33.6
20	11.0	47	21.4
30	13.0	50	19.2
40	20.3	*66.2	*17.4
42	31.6	70	17.4
42.8	85.3	90	18.1
43	$+\infty$		

Blue-opaque. \* Minimum. Yellow-opaque.

This curve, equation (1), has been inscribed in fig. 5, to show the grouping of the observations around it. The minimum is marked at  $a$  ( $t_m = 17.4^\circ$  C.,  $p_m = 66.2$  cm.). Throughout the extent of the figure, it unites two sufficiently flat curves to fairly represent the observations; for this part of the margin, from its exceedingly steep ascent, cannot be traced with precision.

As a whole, therefore, equation (1) has reproduced the complete phenomenon surprisingly well, both as regards the blue-opaque (AB) and the yellow-opaque (BC) margin of the opaque field. No doubt, better agreement could be had on further trial, particularly by varying the point of intersection with the abscissa,  $t=A$ . I shall not, however, do this, since in the present paper the chief datum is the height of the common asymptote ( $p=B$ ) above the abscissa. It is this parameter which expresses the dust-contents of the air, and which fortunately may be obtained without computation by the direct observations presently to be more fully specified.

11. *Artificially Dusty Atmospheres.*—To interpret the above data it is necessary to increase the dust-contents of the normal



atmosphere artificially, utilizing the tube F, fig. 1, containing phosphorus. The results for this case are not without complexity, but the character of the effect produced is obvious at once: it takes but a trace of the phosphorus-tainted air to make the field permanently opaque at all pressures and temperatures not unreasonably high. In other words, the tendency is to drop the blue-opaque curve of the above figures into coincidence with the abscissa. One would surmise that at least the asymptotic portion of the yellow-opaque curve would likewise drop to the abscissa, and this is actually the case, as will be shown presently. By allowing the discharge from F to take place into E through a glass tube only a few millimetres in diameter, while the air-tube C is fully two inches in diameter, I was able to dust the air sufficiently to obtain at least the approximate contours of the corresponding relation of steam-pressure and air-temperature. The data are inscribed in fig. 4, and together they make up the curve P near the axis of temperature. Thus the striking potency of even traces of dust is well exhibited.

Clearly the rudimentary curve P is a member of the same family to which AB belongs, and it is therefore obvious that the whole field between B and the abscissa is a region of temperature and pressure loci \*, each of which corresponds to a particular value of dust-contents. Since, therefore, the accuracy with which the point can be located at any (mean) temperature is about 1 cm., the apparatus ought to register about 40 degrees of dust-contents between normal atmospheric air and the artificial mixture stated. On this scale the variation of the dust-contents of normal air † lies in the interval between 40 cm. and 50 cm. of mercury, remembering that the height of the asymptote (virtually reached at  $28^{\circ}$  to  $30^{\circ}$ ) is taken for registry.

12. To bring out the conditions more fully, however, it is necessary to make supplementary tests both with phosphorus and with filtered air.

If the basket of phosphorus is placed in the tube E (fig. 1)

\* Probably the best method of actually mapping out these curves will consist in using nozzles of different degrees of smoothness. By mere haphazard drilling and polishing of such nozzles, I obtained curves between asymptote 20 cm. and asymptote 50 cm. That these curves will be identical with the corresponding dust-curves is made probable by §16 below.

† Supposing that the possible errors have been correctly apprehended. In experiments made throughout the entire month I was surprised that an apparatus so sensitive to artificial dust should show such slight mean variations of the dust-contents of atmospheric air from day to day. Witness the above curves.

near its mouth *d*, where the air-temperature (in winter) is near the freezing-point, no effect is produced. Thus at  $21^{\circ}$ – $22^{\circ}$  the blue-opaque margin was at 41–42 cm., showing that the oxidation of phosphorus at zero is relatively negligible in spite of the current of air.

If, however, the same phosphorus be placed in the tube EC at *i*, somewhere between the point of confluence and the colour-tube, and where the temperature is say  $20^{\circ}$ , then it is actually possible to obtain the yellow of the first order at steam-pressures less than 1 cm. Thus at  $19^{\circ}$ , the yellow-opaque margin was at 1.2 cm., and the colour persisted with increasing brilliancy at all pressures above this.

For temperatures greater than  $20^{\circ}$ , the tube is yellow at all pressures until eventually above  $35^{\circ}$  all colour vanishes for want of supersaturation.

For temperatures below  $20^{\circ}$ , the tendency is to produce opaque fields. Thus at  $15^{\circ}$  the tube is opaque at all pressures above a few millimetres.

The explanation of this somewhat puzzling behaviour is this: at any given admissible temperature, the effect of phosphorus dust is a change of the colour of the field in the direction from blue through opaque to yellow in proportion as more dust of the given kind is added. Again, the dust-contents of the air passing over a given lump of phosphorus decreases both with the rapidity of the current and with the degree of cold. Hence at higher temperatures than  $20^{\circ}$  brilliant brown-yellow fields are the usual occurrence when the phosphorus lies in the air-tube *i* C. If withdrawn from the air-tube and so circumstanced that its exhalation is diluted with much air (tube F, fig. 1), then any colour may be produced, depending on the degree of dilution. On the other hand, below  $20^{\circ}$  the oxidation takes place more and more slowly, so that only very gentle currents of air can carry off enough dust to produce a yellow field. For strong currents in C there is a double source of dilution, and opaque fields are the rule. In other words, the air now approaches the state AB in fig. 4, so far as dust-contents are concerned.

I have entered into this subject at length because of its important theoretical bearing, seeing that it is necessary to disentangle a series of involved relations.

13. In fig. 6 (diagram), the pair of curves ABC indicates the margin of the opaque field for unusually pure atmospheric air. Above the horizontal asymptote through B there is a symmetrical disposition of browns, oranges, and yellows, the order of colours decreasing upward. Below B the colours are blues, greens, and hues of higher orders. The whole field to

the right of ABC is coloured, merging into colourless ; the field to the left of ABC is opaque.

As the air becomes more and more dust-laden, the yellow territory encroaches on the blue, so that for unusually dusty atmospheric air the pair of curves ABC has changed into ADC.

In the same way the yellows will continue to advance upon the blues for each successive (now artificial) increment of the dust-contents of the air, until eventually the blues have been quite crowded out of the field, and the whole territory is persistently yellow at all temperatures and pressures. In other words, the asymptote of the curve descends with increasing dust-contents, while at the same time the curve BC moves bodily to the right, so that BC finally coincides with the co-ordinate axes of pressure and temperature. This at least is the essential feature of the phenomenon so far as I now understand it. Subsidiary details will be brought forward at some other time.

It is to be remembered that the particular curves, figs. 2 *et seq.*, apply primarily to the particular jet discharging into the given tubes. Nor can any attempt as yet be made to graduate the apparatus ; for a comparison with the Aitken dust-counter is not legitimate, unless it can be proven that any given class of particles \* occurs proportionally to the total number, certainly a hazardous hypothesis. For the present the height of the curve at points above  $28^{\circ}$  (asymptote), expressed in centimetres of mercury (pressure), is the empiric dust-indicator.

14. *Filtered Air.*—A grave difficulty is encountered in using filtered air, inasmuch as the supply cannot be obtained in sufficient quantity without employing very cumbersome apparatus. I have helped myself provisionally by using a tin tube G (fig. 1) with the end *nn* large enough to fit snugly into the air-hole C when the heater is removed. G is filled with cotton throughout about 20 cm. of its length in the usual way. The end *nn* is closed with a sieve of brass wire gauze, while the end *m* is closed with a perforated rubber cork, through which an influx tubulure, *o*, projects. This is connected with an ordinary gas-tank, containing highly compressed air.

When the tube C (fig. 1) is closed with the filter G (no gas passing through it), the field of AA at once becomes clear ; at the same time, however, its temperature rises to the

\* Cf. §14. Evidence is also adduced in my earlier paper (Am. Met. Journ. March 1893, §19) that it is only the smallest of dust particles—*i.e.* particles whose dimensions are limited either way and of the order of a few hundred molecular diameters—which induce coloured cloudy condensation.

boiling-point, and the absence of colour in this case is more the result of insufficient supersaturation than of absence of dust. Now let the compressed air be admitted, so that the tube *AA* is considerably cooled. If the steam-pressure is high enough, and the gas in sufficient quantity, the field first clouds over and then turns quite opaque. Thus at a pressure of 50 cm., and a temperature registered at *t* of 47°, such a result (opaqueness) was obtained. At 30 cm. steam-pressure the field turned cloudy, but not opaque; at 15 cm. no clouding was even apparent. Colours were not observed in any case.

In view of the insufficient air-supply obtained in case of the filter *G*, I replaced it by the form *H*, differing from *G* in having a drum much larger in diameter (length 25 cm., diameter 15 cm.), and special sieves *rr* and *ss*. Similar parts are similarly lettered. Under like conditions, such a filter should supply nine or more times as much air as the other (*G*).

The absorbent cotton inserted between the sieves *ss* and *rr* (the former and the lid being removed, and the latter [*rr*] soldered in place) was carefully laid in layers parallel to *rr*, quite filling the width of the drum. When full to the top, the cotton was compressed by the second sieve *ss*, which thereafter was also soldered in place, the lid with the inlet pipe *o'm'* soldered on, and the space between lid and *ss* filled with loose cotton to catch dirt. The compressed charge between *ss* and *rr* mainly acts as the filter. When not in use it should be heated, so as to be thoroughly dry.

In the first experiments with the filter *H*, compressed air (issuing as usual from a narrow pipe, and at a tank-pressure of about 15 atmospheres) was used as before. Spreading through the filter, the air enters the colour-tube at a much reduced velocity. As the air in the tank is gradually freed from dust by the subsidence of the latter, there is here an additional means of purification. But the method is much too lavish to be practical, even if it be conceded that the filter is actually efficient. The following data were thus obtained for the margin of the opaque field at temperatures comparable with the values in the charts. Colours were not observed:—

Temperature . . . .	20°	21°	22°	23°	33°	Centigrade.
Pressure . . . .	41.5	42	43	44	5.8	Cm. Hg.

In the set of data for 20° to 23° the filter was not so well packed as at 33°. Observations were discontinued for want of gas. I have inserted these data in the chart, fig. 3, at *F* and *F'*. When taken together they suggest a locus of the same nature as fig. 4, *i. e.* implying less curvature in

proportion as the air is less dusty. Bearing this in mind, the margin of the opaque zone at  $20^{\circ}$  for filtered air is not as much above the atmospheric curve as one would anticipate. It follows that the size of the particles producing coloured cloudy condensation in atmospheric air is not necessarily enormous when compared with molecular diameters—an inference which I have already drawn\* both from the character of the colour phenomena and from the conditions of condensation.

15. Having obtained these preliminary results, I attacked the subject on a much larger scale, using an apparatus very similar to fig. 1 (with the phosphorus-tube removed), except that the air, instead of being taken out of the atmosphere at *c* and *d*, passed at those points through two large filters of the type H (fig. 1). A large Root blower, actuated by a one-horse-power gas-engine, forced the air through the system.

Contrary to my expectations, this arrangement remained to the last utterly inefficient. When the blower acted under low pressures, the air entering the colour-tube was insufficient in quantity. For higher blower-pressures and a more rapid current of air †, the evidences of filtration were practically absent. It was easy to trace the increase of dust-contents with the velocity of the current of nominally filtered air, even though high speeds were excluded by the nature of the case. The nozzle of the original steam-jet being 0.16 cm. in diameter, I replaced it by a finer one, 0.09 cm. in diameter, but without advantage. It is noteworthy that for atmospheric air both these jets gave identical results as to the location of the opaque margin near the asymptote. The colours for the fine jet were fainter, and together with the opaque field vanished at a lower temperature, as one would suppose, seeing that only one third as much steam is available in one case as in the other.

The best results for filtered air are, therefore, those of the preceding paragraph. A sufficient degree of supersaturation presupposed, in no case was there an absence of condensation; but as I cannot assert that the air used was rigorously pure, it does not follow that I have reached the conditions ‡ under which the molecules themselves act as condensation nuclei.

\* Amer. Met. Journ. ix. pp. 507, 519 (1893).

† Compare this with the similar experiences of Mr. Aitken, in Trans. Roy. Soc. Edinburgh, xxxv. p. 11 *et seq.* (1888).

‡ The delicate question of purity comes into play in the other researches. Thus condensation apparently without nuclei was produced by Aitken (Trans. Roy. Soc. Edin. xxxv. p. 16, 1888), using the expansion method. R. v. Helmholtz failed to obtain it for exhaustions up to one-half atmosphere (Wied. Ann. xxvii. p. 521, 1886), whereas Aitken's exhaustions were only to three-fourths atmosphere (*l. c.* p. 8).

Were this the case, then the supersaturation at the lower margin of the opaque field, expressed either isothermally as pressure or isopiesticly as temperature, would lead easily to the dimension of steam molecules. For the margin in question is a locus at which the issuing steam condenses as a whole, or in which the vapour contains within itself the conditions \* of condensation.

16. In the absence of my other papers, the last remarks need further elucidation. I have already shown † that the opaque field at any temperature occurs cotemporaneously with the breakdown of the stability of the steam-jet. In other words, whenever at any temperature the velocity of the jet is just sufficient to change steady into edging motion, then an opaque field is observed in the colour-tube. One is therefore amazed to find brilliant browns, oranges, and yellows appearing after the jet-velocity or jet-pressure is even further increased, and the natural inference is that with the occurrence of the opaque field the degree of supersaturation reached is intense enough to cause the steam to condense without nuclei. Conformably with this view of the case, condensation at pressures below the opaque margin is induced by dust, whereas above the opaque margin condensation is independent of dust. Above and below the margin the colour-phenomena are thus different in origin, and experiment bears this out to the extent that the yellows in question, however produced, are not influenced by injections of active dust.

Thus far all is plausible ; but the explanation given receives a rude shock when further observation shows the height of the asymptote to vary enormously (pressure, 20 cm. to 50 cm. of mercury) for different nozzles. Even in one and the same (brass) nozzle the height gradually decreases in the lapse of time in proportion, no doubt, as the smoothness of the nozzle is impaired by continued use (usually sulphur corrosion). Hence the hydraulic phenomenon—*i. e.* the breakdown of the stability of the jet—is the primary occurrence, and the condensation phenomenon follows upon this. It is still possible to patch up the view above stated by supposing supersaturation to be sacrificed with the breakdown of the jet, seeing that the turbulent motion of the now noisy (intermittent) efflux of steam is not such in which one would expect to retain the supersaturated state.

\* Lord Kelvin's well-known equation (*cf.* Maxwell's 'Heat,' chap. xx.) is here made the basis of consideration.

† *Cf.* Phil. Mag. xxxv. p. 315, 1893 ; *cf.* Am. Met. Journ. March 1893, p. 505.

Explanations of this kind are, however, too hazardous to be satisfactory. I therefore resolved to enter into the question thoroughly by exploring what may be called the thermal topography of the steam-jet, *i. e.* the longitudinal and radial distribution of temperature throughout the jet for all actuating steam-pressures, and for as many temperatures of the surrounding air as I could obtain. The data \* thus laboriously gained did not, however, enable me to fashion as trenchant an argument as I had looked for, chiefly because it is difficult, even with the best thermoelectric means, to measure the temperature of the narrowing jet quite up to the nozzle; and it is just here that the region of marked supersaturation is located, as is evidenced by the sensitiveness of these parts (Aitken). It seems expedient, therefore, to postpone decision for the present, merely stating that if the degree of supersaturation (measured isothermally as pressure) necessary for spontaneous condensation can be reached, the data, in virtue of the Kelvin formula, must lead to a new method for measuring the molecular diameter peculiar to water-vapour—a method, moreover, which need not fail for other vapours.

In concluding, it is interesting to advert to the corresponding phenomenon in the case of the solidification of a liquid. I have shown† that in an *isothermal* march the pressure at which a liquid freezes is apt to be much greater than the pressure at which the same (solid) substance again melts. In case of naphthalene, for instance, the magnitude of the lag may reach 300 to 400 atmospheres. One is therefore tempted to seek an analogous explanation for the stated difference of melting and freezing pressures at the same temperature, in the absence of nuclei, postulating a tendency to liquefy (osmotic pressure?) even in solid substance‡, varying with the curvature of the surface. A difficulty, however, now presents itself, inasmuch as a liquid cooled below its melting-point (unlike the corresponding case for vapours) can be kept in a solid vessel without solidifying. Hence the method for measuring liquid molecular diameters which seems to loom into view is not so near at hand.

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\* These are fully given in the Weather Bureau Bulletin cited, which has now been in the press for about a year.

† Barus, Amer. Journ. of Science, xlii. p. 125, 1891. For a full account, see Bulletin of the U.S. Geological Survey, No. 96, p. 83, 1892.

‡ Evidence in favour of the occurrence of solid surface-tension is given by Auerbach (Wied. Ann. xliii. pp. 61, 94, 1891) and others.

III. *On Torsional Oscillations of Wires.* By Dr. W. PEDDIE,  
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*Sketch of Previous Work* †.

THE present subject is part of the more general one—the deformations of a non-rigid solid. That strain, or part of a strain, which disappears wholly on the removal of the distorting stress, is called *temporary strain*: that which is observed after the complete removal of the distorting stress, is called *permanent strain* or *set*, though it may, and usually does, diminish as the time which has elapsed since the complete removal of distorting stress increases. The latter effect, together with the converse effect of the gradual increase of set under continued constant stress, is called *after-action* by the Germans.

In 1835 (Pogg. *Ann.*) Weber investigated the laws of permanent set of a stretched fibre. In 1837 (B. A. Report; see also B. A. Reports, 1843, 1844) Hodgkinson, as the result of experiments on cast iron, came to the conclusion that “the maxim of loading bodies within the elastic limit has no foundation in nature”; that is, permanent set is produced by any stress however small. In 1842 (*Ann. de Chim. et Phys.*) and 1848 (Pogg. *Ann.* Ergbd. ii.) Wertheim observed that permanent set occurred in a *previously undistorted body* as the result of any stress however small; and in 1848 (Camb. & Dubl. Math. Journ.) this limitation to Hodgkinson’s statement was independently pointed out, as a deduction from theory, by Prof. James Thomson. On the other hand, a body previously distorted in a given sense may be again distorted to a smaller, or the same, extent in the same sense without the production of new permanent set.

Between 1858 and 1862 G. Wiedemann made statical experiments on the torsion of rods, in the course of which he verified Wertheim’s observation; and in 1880 (Phil. Mag. vol. ix.) he published the results of more extended experiments of the same kind. One of these results is that, after repeated twistings, alternately in opposite directions, by a given couple, the set of a rod becomes constant; and, if the rod be again twisted, by increasing couples, in the direction of the last twist, the strain (measured from the position of set) is

\* Communicated by the Author, having been read before the Royal Society of Edinburgh, December 18, 1893.

† This sketch is a mere outline. Fuller references will be found in the papers quoted.



practically proportional to the stress so long as the original value of the couple is not exceeded. Another is that the reversed couple produces a greater strain, measured from the last set, than does the equal direct couple; the difference in this case corresponds to the change of zero produced by the reversal of the couple—that is, to the set. Again, by repeated reversals of twist under a given couple, the total torsion and the set diminish to fixed minimum values. Also, in the case of torsion in one direction, the values of the total torsion and of the set increase at increasing rates as the couple increases, and the latter relatively at a greater rate than the former: these values for a given couple increase to maxima by repeated applications of the couple, and this increase is also relatively greater in the set than in the total torsion. Wiedemann remarks that the approach of the position of final set to that of final total torsion in this case is a phenomenon of the same kind as the narrowing of the limits of total torsion and of set by repeated reversals of a given couple; the only difference is that the negative couple is zero. He calls the process by which the wire is brought into the steady state as regards total torsion and set the process of *accommodation*.

In 1865 (Proc. Roy. Soc. Lond.) Lord Kelvin described results obtained from the observation of torsional oscillations of wires. He discovered the phenomenon of “elastic fatigue,” and found that the diminution of the range of oscillation, per equal number of oscillations, followed the law of compound interest when the range was very much smaller than the palpable limits of elasticity. Tomlinson’s observations (Phil. Trans. 1886) support this conclusion.

#### *Present Observations and Results.*

So far as I am aware, no attempt has been made to find the law of decrease of the range of oscillation when it is so large that it is accompanied by marked set—set which may amount to a large fraction of the total range. Lord Kelvin’s observations were purposely made upon small oscillations in order to avoid the disturbances which are introduced when the oscillations are large. Because of the known intimate dependence of the instantaneous state of strain of a body under given stresses upon all the previous strains to which it has been subjected, it might be supposed that it would be absolutely impossible to deduce with certainty any general law of decay of large oscillations. In other words, any systematic arrangement of conditions might seem to be unattainable because of the possible intrusion of arbitrary and uncontrollable, perhaps even untraceable, conditions. As a matter of fact, I have

found that, in all my observations hitherto made, such arbitrariness is notably absent ; and I have been able to obtain an extremely accurate empirical formula for the representation of the results.

The results here given refer only to a single iron wire whose extremities were soldered into holes drilled axially in stout brass rods. The length of the wire was 89.1 centim., and its diameter was 0.1011 centim. The one rod was firmly clamped in a vertical position, with the wire suspended from it ; and to the other rod was attached, symmetrically and horizontally, a heavy lead ring of considerable moment of inertia. In performing the observations, one experimenter increased the torsional oscillations of the system up to a predetermined maximum, taking care to avoid as far as possible any swing of the system like that of an ordinary pendulum. Whenever the required maximum oscillation was attained, the system was left to itself, except in so far as any marked swing of the latter kind was damped out in such a way as not to interfere, by friction or otherwise, with the torsional oscillations. Another observer commenced at once to take readings of the maximum elongation by means of a telescope placed a few yards off. The scale was fastened round the outer circumference of the lead ring, and a fixed pointer was placed close in front of it. At first readings were taken at the end of each complete oscillation ; subsequently, as the time-rate of decay of the oscillations became less, readings were taken at the end of two, three, five, or more, complete oscillations. A curve was then plotted with the scale-readings as ordinates and the number of swings as abscissæ. The oscillations were found to be almost isochronous, so that the axis of abscissæ was practically a time-axis. In almost all cases the curve showed traces of ordinary pendulum oscillations, but a smooth curve could easily be drawn on the average through the observed points so as to avoid all such irregularities. It would serve no useful purpose to give here the full details of each experiment. Their general nature will be seen from the curves shown in fig. 1, and the special data given in Table II. will be found sufficient for each. In fig. 1 the curves give the data obtained from observation, and the points show positions calculated from the respective equations in Table I.

It was found that equations of the form

$$y^n(x+a)=b, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $a$ ,  $b$ , and  $n$  are constants, applied with great accuracy in each case Table I. gives details on this point.

The curves C, G, H, I, J, K are omitted as they were made with an entirely different object and the readings did not cover the same range.

The actual value of the constant added to  $x$  depends upon the interval which elapses after starting the experiment until the first reading is taken. Thus the fact that in B this constant is greater by about unity than the similar constants in D, E, F, while the first reading in B is much less than the first readings in D, E, F, points to the conclusion that the first reading in that curve was taken one oscillation later than the first readings in the latter. We should therefore expect that the value will be small when the initial range is large, as in M. The values of the other two constants in the equation for M are much increased relatively to their values in the preceding equations—a fact which illustrates the dependence of the action at any stage upon the previous treatment of the wire. The decay of the oscillations is at first more rapid, afterwards more slow, than in the preceding experiments.

In P the phenomenon of elastic fatigue is very apparent. The conditions were practically the same in this experiment as in, for example, E, F, and O, with the exception that in P the wire was kept oscillating to the maximum extent for about half an hour before the observations began. The rate of decay of the oscillations is immensely increased at all the observed values of the range.

Putting aside the special experiments M and P, we find that, after the wire had once reached a steady state (in B), the steady state was maintained day after day; so that it was easy to repeat an experiment under practically the same conditions. Even the exceptional treatment in M did not prevent the return of the wire to its old condition before the experiment on the following day was performed. In only one case,  $L_1$ , is there any exception, and this may have been due to a difference of temperature.

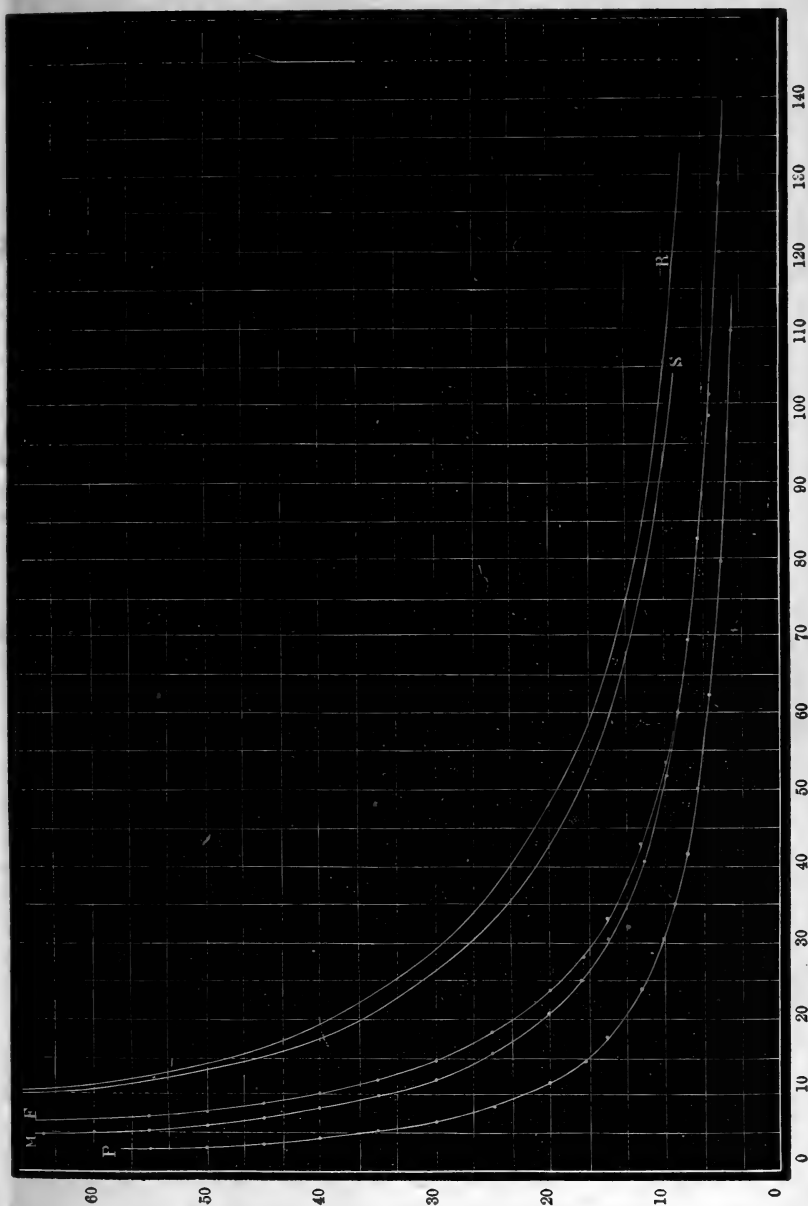
In the earlier experiments the initial range is said to be over 100. No exact record was kept, but the excess was considerable; the actual angle was probably about 125. In the experiment O the angle was *maintained* steadily at 125 for some time before the wire was let go and the observations were begun. The constants were not altered by this treatment; and this seems to indicate that the “after-action” under steady stress has little or no effect in these experiments, which are made under otherwise similar conditions.

The experiment C was performed on the same date as B; so that D was performed after the wire had been at rest for

TABLE I.

Curve.	Date.	Equation.	Initial Range.	First Reading.
A .....	5-7-93.	$y^{1.05}(x+6.5)=574.$	Over 100.	66.5.
B .....	7-7-93.	$y^{1.18}(x+7.5)=802.$	.....	53.5.
D .....	10-7-93.	$y^{1.18}(x+6.6)=802.$	Over 100.	Nearly 70.0.
E .....	10-7-93.	$y^{1.18}(x+6.4)=802.$	Over 100.	65.0.
F .....	10-7-93.	$y^{1.18}(x+6.4)=802.$	About 125.	65.0.
L <sub>1</sub> .....	14-7-93.	$y^{1.18}(x+7.3)=842.$	About 125.	65.0.
L <sub>2</sub> .....	14-7-93.	$y^{1.18}(x+6.7)=802.$	About 125.	66.0.
M .....	17-7-93.	$y^{1.32}(x+4.4)=1074.$	About 175.	68.5.
N .....	18-7-93.	$y^{1.18}(x+6.6)=802.$	Over 125.	67.0 fully.
O .....	18-7-93.	$y^{1.18}(x+7.0)=802.$	125.	61.0 fully.
P .....	18-7-93.	$y^{1.4}(x+2.6)=761.$	About 125.	About 55.

Fig. 1.



three days. Between the experiments F and L<sub>1</sub> experiments were performed every day—twelve experiments in all, some with large, some with small, oscillations.

### *Test of the Empirical Formulæ.*

In the following table a comparison is made of observed results in each experiment with the results calculated from the formulæ. In the upper row are given values of  $y$  common to all the experiments.

These figures show that the correspondence between the observed results and the results derived from the empirical formulæ is very close, and that it holds throughout a large range of values of  $x$ . The curves in fig. 1 show this even more clearly.

All the results given in Table II. for each experiment with the exception of P were observed within ten minutes after starting the oscillations. All the results given for P were observed within thirteen minutes. Within these time-limits, therefore, the quantity  $n$  in the equation is practically constant. Yet, since from that table we see that the value of  $n$  may diminish from 1.32 to 1.18 in the course of twenty-four hours, we cannot assume that  $n$  will not vary in amount in any one experiment until the vibrations cease to be observable. As a matter of fact, it does so vary.

### *Variations in the Value of $n$ .*

From Table I. it appears that when a fresh wire is oscillated with a given initial maximum range on different occasions, the quantity  $n$  at first increases in magnitude and ultimately reaches a value which remains constant so long as the treatment of the wire from day to day is fairly uniform. This value is exceeded if the given initial range be exceeded, or if the wire be "fatigued" by long-continued oscillation; but the previous steady value of  $n$  is soon reacquired.

If the empirical formula above used be correct, any two values of  $y$  corresponding to a constant difference in  $x$  must satisfy the condition

$$\frac{y_1^n - y_2^n}{y_1^n y_2^n} = \text{constant.} \quad . . . . . (2)$$

If too large a value of  $n$  be used in this equation, the value of the quantity on the left-hand side will increase when the values of  $y_1$  and  $y_2$  decrease. If too small a value be used, the quantity will decrease when  $y_1$  and  $y_2$  decrease.

TABLE II.

Curve.	$x+a$ .	65.	60.	55.	50.	45.	40.	35.	30.	25.	20.	17.	15.	12.	10.	9.	8.	7.	6.	5.	4.
A.	Obs. ... Calc. ...	..... .....	8.0 7.7	8.5 8.5	9.2 9.3	10.2 10.5	11.5 11.7	13.3 13.7	16.0 16.0	19.6 19.5	24.6 24.7	28.9 28.5	33.3 33.2	42.0 42.1	51.6 51.0	57.6 57.1	65.6 64.5				
B.	Obs. ... Calc. ...	..... .....	..... .....	..... .....	8.0 7.9	8.9 8.9	10.3 10.3	12.1 12.1	14.9 14.5	18.2 18.0	23.4 23.4	28.1 27.6	32.4 32.9	42.5 42.7	53.0 53.0	60.0 60.0	69.5 69.0				
D.	Obs. ... Calc. ...	..... .....	7.4 7.1	8.0 7.9	8.9 8.9	10.3 10.3	12.1 12.1	14.8 14.5	18.3 18.0	23.3 23.4	28.0 27.6	32.1 32.9	41.6 42.7	52.6 53.0	60.4 60.0	69.0 69.0					
E.	Obs. ... Calc. ...	..... .....	7.0 7.1	7.8 7.9	8.7 8.9	10.0 10.3	11.9 12.1	14.4 14.5	18.1 18.0	23.4 23.4	28.0 27.6	32.7 32.9	42.5 42.7	53.4 53.0	60.4 60.0	70.4 69.0					
F.	Obs. ... Calc. ...	..... .....	7.0 7.1	7.8 7.9	8.7 8.9	10.0 10.3	11.8 12.1	14.5 14.5	18.0 18.0	23.3 23.4	27.8 27.6	32.1 32.9	42.0 42.7	52.4 53.0	60.4 60.0	70.4 69.0					
L <sub>1</sub> .	Obs. ... Calc. ...	..... .....	8.0 7.4	8.6 8.3	9.5 9.3	10.8 10.8	12.7 12.7	15.4 15.2	19.1 18.9	24.6 24.5	29.4 29.0	34.3 34.5	44.7 44.8	55.8 55.6	62.8 63.0	73.3 72.4					
L <sub>2</sub> .	Obs. ... Calc. ...	..... .....	7.4 7.1	8.0 7.9	8.8 8.9	10.2 10.3	12.1 12.1	14.7 14.5	18.4 18.0	23.6 23.4	28.7 27.6	33.2 32.9	43.1 42.7	53.3 53.0	60.0 60.0	69.7 69.0					
M.	Obs. ... Calc. ...	4.60 4.35	4.8 4.8	5.2 5.3	5.9 6.1	6.9 7.1	8.1 8.2	9.80 9.85	12.0 12.0	15.1 15.3	20.5 20.5	25.0 24.8	29.6 30.1	39.7 40.4	51.0 51.4	58.4 59.0	69.4 69.0	81.4 82.3			
N.	Obs. ... Calc. ...	..... .....	7.3 7.1	7.9 7.9	8.8 8.9	10.0 10.3	11.9 12.1	14.5 14.5	18.0 18.0	23.6 23.4	27.2 27.6	32.3 32.9	42.6 42.7	52.9 53.0	60.1 60.0	69.1 69.0					
O.	Obs. ... Calc. ...	..... .....	7.4 7.1	7.9 7.9	8.7 8.9	10.2 10.3	11.7 12.1	14.4 14.5	18.0 18.0	23.4 23.4	28.3 27.6	32.5 32.9	42.5 42.7	53.0 53.0	60.0 60.0	70.0 69.0					
P.	Obs. ... Calc. ...	..... .....	2.7 2.8	3.1 3.2	3.5 3.7	4.1 4.3	5.2 5.2	6.6 6.4	8.8 8.4	11.6 11.7	14.2 14.0	17.1 17.2	23.6 23.4	30.0 30.3	33.6 35.1	40.6 41.4	49.6 49.9	61.6 61.9	80.6 79.9	109.0 109.3	

We shall apply this test to the results of experiment C (not given in Table I.), in which the initial range was only about 80, and 300 oscillations were observed. The values of  $y$  for which  $x$  has the values 10, 20, 30, 40 are respectively 44.9, 31.9, 25.3, and 21.1. The values of the left-hand side of (2), with  $n=1$ , for the stretches of  $x$  10-20, 20-30, 30-40, are respectively 0.0091, 0.0082, 0.0078. Hence the true value of  $n$  for this part of the curve is greater than unity. The values of  $y$  for which  $x$  has the values 80, 160, 220, 300 are respectively 13.5, 7.9, 6, 4.4. The values of the left-hand side of (2), with  $n=1$ , for the stretches of  $x$  80-160, 220-300, are respectively 0.052 and 0.061. Hence, in this part of the curve, where the oscillations are small relatively to the initial range, the true value of  $n$  is less than unity. If in this part of the curve we take  $n=0.5$ , we get, instead of 0.052 and 0.061, the quantities 0.083 and 0.068 respectively; so that  $n$  exceeds 0.5.

We shall next apply equation (2) to the results of experiments R and S, performed at the dates 15-11-93 and 17-11-93 respectively. As in the experiments given in Table I., the initial range was about 125. Previous to the former date the wire had been left at rest with the lead ring appended since the date 19-7-93, *i. e.* during a period of nearly four months.

In the curve R the values of  $y$  for which  $x$  has the values 10, 20, 30, 40 are respectively 38.8, 29, 22.9, 18.8. The values of the left-hand side of (2), for  $n=1$ , over the three stretches of  $x$  10-20, 20-30, 30-40, are respectively 0.0087, 0.0092, 0.0095. For  $n=0.5$  the numbers are 0.0025, 0.0024, 0.0021. Hence  $n$  is greater than 0.5 and less than unity.

In the curve S, at the same values of  $x$ , the values of  $y$  are 36.6, 26.9, 21.1, 17.3; and the values of the left-hand side of (2) are 0.0098, 0.0102, 0.0104. Hence  $n$  is less than unity. The differences of these numbers are 0.00022 and 0.0002. The corresponding differences in R are 0.0005 and 0.0003. Hence  $n$  is larger in S than in R.

### *The "Compound Interest" Law.*

There can be no doubt that, when the range of oscillation is "much smaller than the palpable limits of elasticity," the decrease of range per oscillation bears a constant ratio to the range itself. This was first shown by Lord Kelvin and, more recently, was confirmed by Tomlinson. When the range is increased this law no longer holds, the logarithmic decrement becoming larger.

In experiment C the observations were continued for a much longer time than in any other experiment, yet the stage



at which the logarithmic decrement becomes constant was not reached. The values of  $y$  for which  $x$  had the values 80, 120, 160, 180, 200, 220, 260, 300, were respectively 13.5, 10, 7.9, 7.2, 6.6, 6, 5, 4.4. The values of the differences of  $\log y$  at the extremities of the stretches of  $x$  80-160, 120-200, 180-260, and 220-300, were respectively proportional to 23, 18, 16, and 13. There is no approach to constancy, although the average decrease of the range per oscillation during the last 40 oscillations was only one three-hundredth part of the average range during these oscillations.

The point will be considered further subsequently.

#### *Approximate Isochronism of the Oscillations.*

An experiment was made, immediately after the performance of experiment M, to determine the period of oscillation over different ranges. The numbers in the first column below, when multiplied by 5, give the initial scale-readings: in the second column are given the corresponding times occupied by the next ten oscillations, the unit being the second. In addition the zero was occasionally read, the values being given in the third column.

5.48	79.0	3.36	5.50	78.4	
5.84	78.8		5.12	79.0	
5.30	78.5	3.36	4.95	78.8	3.49
7.15	79.0		13.90	79.8	
6.05	78.5		8.00	79.4	
5.45	78.5	3.36	6.15	79.0	
14.90	79.7		4.80	78.5	
6.60	78.5	3.43	4.50	78.5	
11.80	79.5		16.50	80.2	
7.60	79.1	3.44	7.80	79.3	
13.20	80.0		4.07	79.2	3.49
7.65	80.0		17.00	80.4	
6.08	79.8		7.50	79.5	
			4.23	78.8	3.49

Despite the irregularities inseparable from the conditions of the experiment, it is evident that the period, while nearly constant, increases slightly as the range increases.

#### *Damping due to the Viscosity of Air.*

In one experiment the surface of the oscillating part of the apparatus was more than doubled by placing light sheets of rough paper on the top of the lead ring. It was found that this did not produce the slightest difference in the observed results. Thus the decay of the oscillations is not appreciably affected by the viscosity of the air.

*Kelvin's and Wiedemann's Theories.*

Lord Kelvin said that the decay of the oscillations might be due to viscous resistance, *i. e.* resistance to change of shape depending on the rate of change, in which case the elasticity is perfect within the limits of the experiment. On the other hand he remarked that, if it were due to dependence of the elastic resilient force on previous conditions of strain, the phenomenon would be continuous with imperfectness of elasticity, and this was indicated to some extent by the phenomenon of "fatigue."

His final experiments were made with small distortions, within the palpable limits of elasticity, to test the former theory. The loss of energy per vibration was greater than could be accounted for by dissipation ensuing on change of shape of an elastic solid, and it was also immensely greater than that due to resistance of the air. He considered also that the results showed a loss of energy much greater than any that could be accounted for by imperfection of elasticity.

Though the compound-interest law was precisely that which would arise from viscous resistance, yet, in that case, the logarithmic decrement should vary inversely as the period; but this was far from being so. Tomlinson finds that the decrement is nearly independent of the period in the more "non-viscous" metals, and that it increases markedly with the period in other metals. Kelvin remarked that the result was such as might be due to "after-action" or imperfection of elasticity.

Wiedemann's statical observations showed that a wire which had once been twisted behaved in quite different ways according as it was twisted to one side or the other of its existing position of equilibrium; whence he concluded that "the hypothesis according to which the decay of torsional oscillations is due to internal friction depending on the velocity alone, can no longer be maintained." Nor could the elastic after-action alone account for it. He then stated his own theory as follows:—Let the wire be "accommodated" by frequent rotations to and fro (see the account of his experimental results on p. 37), and therein at last be temporarily twisted in the positive direction, describing an angle  $+\alpha$ , while the molecules may be rotated so that the lower ends of their axes, looked at from the axis of the wire, describe an angle  $+\alpha$ , say to the left. The direction of this rotation follows from my magnetic experiments. If the wire be slowly brought back into the permanent torsion-position  $+b$ , the axes of the molecules will retain a portion  $+\beta$  of their rota-

tion to the left. If the wire now receives an impulse in the positive direction, which again elongates it up to  $+a$ , according to the laws of perfect elasticity it will swing back again to the position  $+b$ . If it now swings beyond this position farther to the right, and if the molecules in their rotation had no friction on one another at all to overcome, it would arrive at the elongation  $-a$ , since the same force that twists it from  $+b$  to  $+a$  twists it in the contrary direction from  $+b$  to  $-a$ , while the axes of the molecules would be rotated just as far ( $-a$ ) to the right as previously to the left. Again, with perfect elasticity the wire would go back to the position  $-b$ , in which the molecules would be rotated  $-\beta$ , and so forth. The to-and-fro motions of the wire, between  $\pm a$  and  $\pm b$ , are perfectly elastic; therefore the performances of work in the swingings outwards and the swingings back again must, within these limits, completely compensate one another. In fact, however, there results a diminution of the amplitudes of oscillation; hence the loss of *vis viva* therein can only correspond to the work which is expended for the alteration of the positions of equilibrium, or the rotation of the molecules from  $+\beta$  to  $-\beta$ , which determine it.

### *Theory of the Present Results.*

The kinetic theory of the viscosity of gases, as developed by Maxwell, asserts that viscosity is due to interchange of momentum between relatively-moving portions of the substances—this interchange being effected by the passage of molecules from one portion to the other. In the same way the viscosity of liquids is explained. There is essentially a passage of molecules from one group to another. Such passage does not take place in a perfectly elastic solid; but there may still be interchange of momentum in the relative motion of the constituents of a group, and therefore true viscosity in a solid. Yet, if the potential energy of deformation of a group is large in comparison with the kinetic energy of average relative motion of the constituent molecules of the group—a condition which holds in the case of the torsional vibrations of a fine metallic wire to the free end of which is attached a mass of great moment of inertia—it seems certain that the energy dissipated by true viscosity will be small in comparison with the energy dissipated in the breaking down of molecular groups (as in Maxwell's theory of a molecularly constituted solid), should such rupture take place to, possibly, a small extent only.

Wiedemann seems to regard the loss of energy as due to the work done in rotating the molecules from one position of

stable equilibrium to another, that rotation causing, in its turn, the permanent relative displacement of the molecules which occurs in the "set:" and this, of course, is quite a plausible hypothesis. In the homogeneous permanent torsional strain the final configuration of a given group of molecules is essentially similar to the initial configuration; yet we may, since a position of unstable equilibrium has been passed, say that the old configuration has broken down and that a new one has been formed; so that the loss of energy may be ascribed to the work done in breaking down molecular configurations.

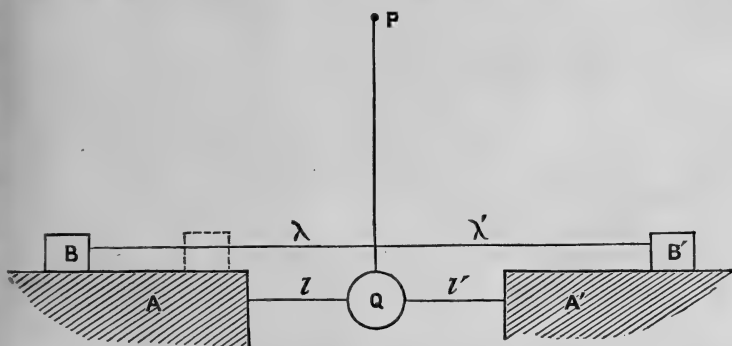
There seems to me to be no need to ascribe such a special type to the rupture of the configurations. On the contrary, I think it more likely that the permanent molecular rotation is a consequence of the permanent set which ensues on complete rupture of configurations—*i. e.* rupture in which molecules in given configurations part company, new groups being formed. It appears to be most probable that the loss of energy in this total rupture greatly exceeds, group by group, the loss due to the cause which Wiedemann contemplates.

Such total rupture takes place in all liquids and in plastic solids; and, by analogy, we conclude that it takes place in all solids to a greater or less extent. Indeed we do not need to rest upon analogy. The evaporation of ice below the freezing-point is due to such rupture; and so, probably, as has been remarked, is the characteristic smell of metals, such as freshly cut copper or iron. At a given temperature, the molecules in a given configuration are in rapid motion with a certain average speed, the actual speed of a molecule being sometimes greatly in defect, sometimes greatly in excess, of this average. When the excess is sufficiently great, the molecule will pass beyond the range of the molecular action of the remaining constituents of the group, rupture of the configuration will occur, and the potential energy of deformation will be transformed into heat energy. In a sufficiently long interval of time such rupture *must* occur, according to the kinetic theory. In a given state of strain it occurs more readily the higher the temperature; at a given temperature it occurs more readily the greater the strain.

It is easy to see that, if a molecule is under directional control by molecular forces, rotation will in general ensue on rupture of a given group. A dynamical illustration will make this plain.

Let PQ represent a pendulum, with a massive bob Q, supported at the point P. Let the pendulum be situated

symmetrically between the rigid fixed blocks A, A', to which it is attached by equal and similar elastic cords  $l, l'$ ; and let the pendulum be attached also by equal and similar elastic cords  $\lambda, \lambda'$ , to the rough movable blocks B, B', which rest, symmetrically with regard to P Q, upon A, A'. So long as B, B' are not displaced the equilibrium position of P Q will not be altered; but if the bob be moved to the right to such an extent as to move the block B into the position indicated by the dotted lines, so that the cord  $\lambda$  becomes slacker, the



equilibrium position will change. The slackening of the cord  $\lambda$  corresponds to the removal of a molecule from a given configuration. The displacement of the equilibrium position corresponds to the set of the molecule P Q. There is change of relative position of Q, A, A', and B', and there is also rotation of P Q from its old direction. The change which takes place in one group is shared by all other groups which are in direct or indirect connexion with that group. This could be shown in the model by attaching P Q by elastic cords to other pendulums. In this way the whole system takes a set.

Displacement of Q from the new position of equilibrium towards the right will take place strictly in accordance with Hooke's Law so long as the former maximum displacement is not exceeded. The old maximum force will be needed to cause the original maximum displacement to the right, but the actual displacement which it causes is now measured from the new equilibrium position. An equal force applied in the opposite direction shifts the equilibrium point back to its old situation, and gives a maximum displacement to the left, from this point, equal to the former maximum to the right. As regarded from the second equilibrium position to the right, the system resists more strongly displacements farther to the

right than it resists equal displacements to the left. These facts illustrate Wiedemann's experimental results with regard to the torsion of wires.

Consider the wire in its initial undisturbed condition, or in any condition of equilibrium with set provided that the next torsion is to be oppositely directed to that which was last performed and which produced the set. If the wire be now twisted through an angle  $\theta$ , and if, during that twist, no configurations break down, the potential energy will be represented, in accordance with Hooke's Law, by the expression

$$V = \frac{1}{2} k \theta^2,$$

where  $k$  is a constant. If there is rupture of molecular groups, the potential energy will fall short of the above amount by a quantity which we shall assume to be proportional to a power of the angle. Thus we get

$$V = \frac{1}{2} k \theta^2 - p \theta^m. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In those cases in which the loss of energy, per outward swing, is small in comparison with the total energy, so that the set is negligible in comparison with the total range, the loss is practically equal to  $k \theta d\theta$ . Hence (3) takes the form

$$-k \theta d\theta = p \theta^m dt, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where  $dt$  is the time of an outward swing. The integral is

$$\theta^n(t + t_0) = b, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $b$  and  $t_0$  are constants, and  $n = m + 2$ .

This is exactly our empirical equation (1); which we thus derive as an approximate consequence of the theory that the loss of energy is due to the rupture of molecular configurations, and is proportional to a power of the angle of torsion.

A glance at the curves in fig. 1 will show that, in the steeper portions, the drop of angle per single swing is not really negligible in comparison with the range, though, even in the steepest portions, it does not exceed one tenth part of the range and rapidly diminishes as the range decreases. Hence we cannot expect the values of  $n$  which hold throughout those portions of the curves which are dealt with in Table II. to hold at still smaller angles of distortion. The value of  $n$  which holds approximately over a considerable stretch of a curve where the angle is large will, quite apart from after-action, be greater than the value which holds over a considerable stretch where the angle is small.

#### *Deduction of the Compound-Interest Law.*

In experiment C the value of  $n$  decreased, as time went on, from a value greater than unity to a value less than unity.

If, in equation (4), we put  $m=2$ , equation (5) takes the form

$$\theta = \theta_0 e^{-at},$$

which expresses the above law. This law therefore follows from our theory if we suppose that  $n$  decreases in value to the limit zero; and the theory shows that the decrement of energy per swing then follows the compound-interest law—just as the decrement of angle does.

### *Explanation of After-action.*

When a wire is held in a state of torsion under a constant couple, some of the less stable molecular groups will in time break down, and so the strain slowly increases. If it be held in a given state of strain, this gradual rupture of groups necessitates a slow diminution of the couple. On the removal of the couple, the wire remains in a state of internal stress because of the set. Consequently the gradual rupture of groups produces a slow diminution of set; for the strongest groups remain unbroken in the original deformation, and, in any ordinary experiment, the groups which break form a small fraction of the whole. This is Maxwell's explanation.

The after-action takes place with comparative rapidity at first: afterwards it goes on more slowly. It takes place more and more completely the longer the strain is continued, and requires proportionally longer maintenance of an equal reverse strain to undo it. Hence, if a wire be twisted first to the right through a given angle for a long time, then to the left through an equal angle for a short time, and be then gradually put into the position of set, we should expect that the set would change (as it does) first in the sense of recovery from the second strain, and finally in the sense of recovery from the first strain.

### *Conditions of Maximum and of Zero Resilience.*

From equation (3) we obtain

$$-\frac{dV}{d\theta} = -k\theta + mp\theta^{m-1},$$

$$\text{or, say,} \quad = -k\theta + k'\theta^{n+1},$$

$$\text{and} \quad -\frac{d^2V}{d\theta^2} = -k + k'(n+1)\theta^n.$$

Hence we see that there is angle of maximum resilience given by

$$\bar{\theta}^n = \frac{k}{k'} \frac{1}{(n+1)}, \quad \dots \dots \dots (6)$$





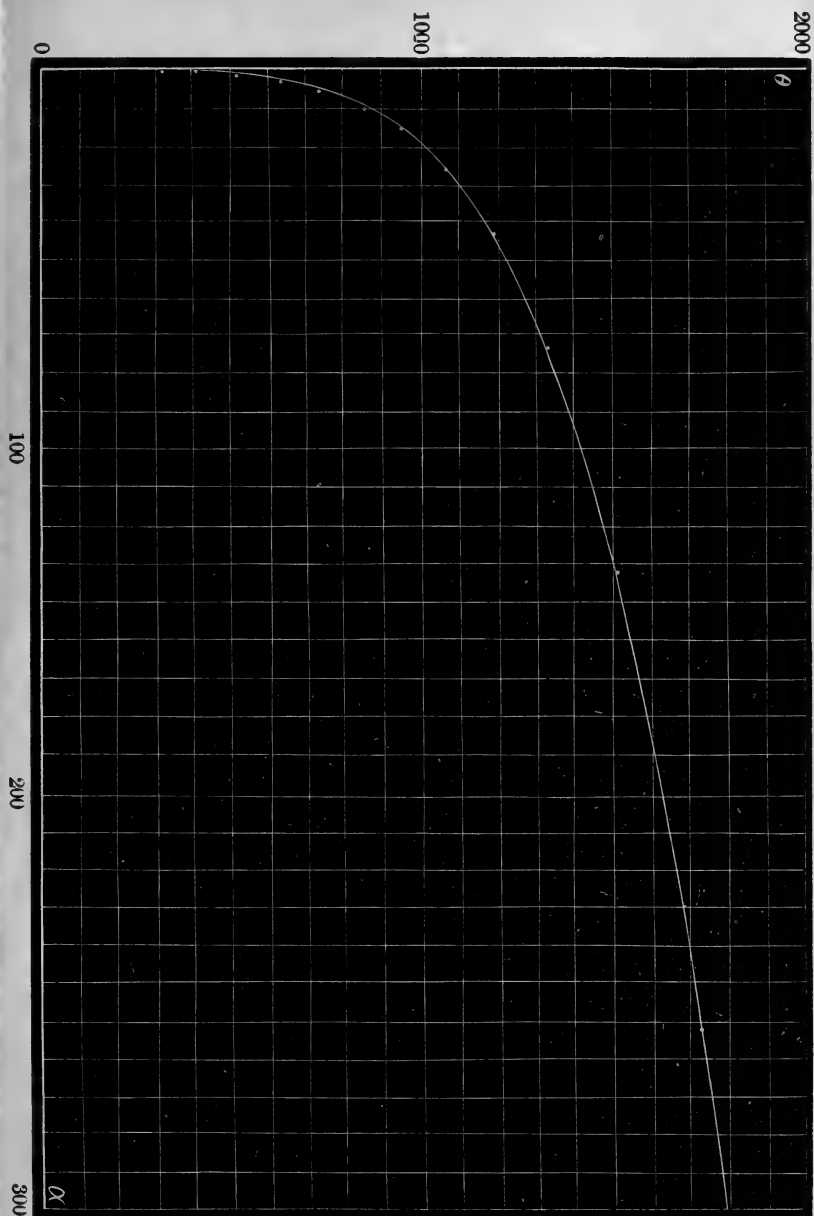


Fig. 2.

*Period of Oscillation.*

The potential energy of the system is

$$V = \frac{1}{2} k \theta^2 - p \theta^m.$$

The kinetic energy of the system oscillating as a whole is

$$\frac{1}{2} I \dot{\theta}^2,$$

where  $I$  is the moment of inertia; and the second term in the expression for  $V$  represents kinetic energy of molecular motion. So the total kinetic energy at the angle  $\theta$  is

$$T = \frac{1}{2} I \dot{\theta}^2 + p \theta^m.$$

Hence we have

$$I \dot{\theta}^2 + k \theta^2 = \text{constant},$$

which shows that the motion outwards is simple harmonic motion as reckoned from the origin; but it is only so in virtue of the condition that the defect of the potential energy from the value that it would have in accordance with Hooke's Law is due to its transformation into a kinetic form. The periods of the outward swing from zero and of the inward swing to the position of set, on the assumption that  $k$  does not change, are each equal to

$$\frac{\pi}{2} \sqrt{\frac{I}{k}}.$$

Wiedemann's statical experiments show that after the few preliminary applications of the maximum twisting couple necessary to fix the set,  $\theta - \alpha$  varies almost in accordance with Hooke's Law, and that the slight difference is in the direction of too great magnitude as the torsion increases: and Tomlinson has shown that great permanent torsion decreases the torsional elasticity. These facts may indicate that  $k$  is slightly decreased at the greater torsions, in which case the period of oscillation will slightly increase as the range is increased.

*Concluding Remarks.*

The experiment A was not the first made with the given wire, though it was the first made with it under the stated conditions of length &c. Thus, in A the wire was in a fatigued condition relatively to its condition in the experiments R and S.

It has been found by Kelvin and Tomlinson that, in the case of small ranges, the rate of decrease of range per oscillation is practically constant for all periods of oscillation in

the less viscous metals and increases with the period in other metals. According to the above theory this is due to the fact that a given state of stress is continued longer, so that the molecular configurations have more opportunity to break down.

If the theory were pushed to the extreme in its application to Wiedemann's results on torsion and set above quoted, we should find that  $\bar{\theta}=2400$ , and that the couple necessary for zero resilience was fully double the maximum couple employed by Wiedemann (that corresponding to  $\theta=1725$ ).

Various deductions might be drawn from the theory in connexion with the observed values of the constants in the empirical equations. I do not think that such deductions would be of any value except in connexion with a much wider experimental basis than that furnished above. I hope soon to be able to communicate the results of further observations.

#### IV. *On the Mechanism of Electrical Conduction.*—Part I. *Conduction in Metals.* By CHARLES V. BURTON, D.Sc.\*

1. **T**HE view of electrical conduction which it is here my object to explain receives general support from more than one consideration; for it leads to the conclusion that deviations from Ohm's Law must be quite inappreciable in the case of metallic conductors, and it goes far to explain, I think, why metals are so much less opaque than their ordinary conductivities would lead us to infer. But it is not alone on such considerations that we have to rely, for, as it seems to me, the main conclusions are capable of exact demonstration; and accordingly it would appear most convenient to commence with a few simple theorems, seeking afterwards to account for known phenomena by means of our definite results.

##### 2. THEOREM I.

*In a region containing matter, there may be (and probably always are) some parts which are perfect insulators and some parts which are perfect conductors; but there can be no parts whose conductivity is finite—unless every finitely conductive portion is enclosed by a perfectly conductive envelope.*

Before proceeding to the proof of this theorem, it may be remarked that the presence of the last clause in no way modifies any application of our result, since the space within a perfectly conductive envelope is completely shielded from

\* Communicated by the Physical Society: read April 13, 1894.

the influence of external charges, currents, or magnets. In the present state of science, indeed, such words appear necessary to the completeness of demonstration, but they do not need to be considered in any of our deductions from the theorem, and for my own part I am persuaded that in reality there is nothing corresponding to the possibility which they suggest.

Consider now the case of any body whatever, at any temperature other than absolute zero. We know that electromagnetic radiations will spread out into the ether surrounding the body, and we must suppose that the intermolecular spaces within the body are also traversed by electromagnetic disturbances. Let us suppose then, for a moment, that in the molecules of the body there are some finitely conductive portions which are *not* enclosed in perfectly conductive envelopes. The electromagnetic disturbances will give rise to currents of conduction in these portions, and accordingly energy will be degraded into a form which is *not heat*, since it consists, not in the motion or relative positions of molecules or appreciable parts of molecules, or in electromagnetic disturbances of the intervening ether, but in something *much more fine-grained*. We shall thus have a *continual degradation of heat into energy of a lower form*; for the electromagnetic "damping" of the finitely conductive bodies involves a continual drain on the energy of internal radiation, and hence indirectly on the energy of the molecules, so that heat will be automatically dissipated in the interior of the body. This process, in which the radiative molecules are continually imparting to the ether more energy than they receive in return, may be compared to the surface cooling of an isolated body which radiates towards colder surroundings.

Even if we suppose the finitely conductive bodies to be extremely small and their conductivity to be either extremely small or extremely great, it is not hard to see that the rate of absorption of heat must be tremendous; and when we consider (for example) the effect which even a very slow absorption, continued for millions of years, would have had on the temperature of our planet, we must admit that the absence of that dissipation of heat implied in the denial of Theorem I. has been established with an exactitude almost unparalleled. Thus the theorem is established.

3. In connexion with this result we are reminded that Poisson's theory of dielectrics requires the molecules of insulating substances to possess some conductive portions, though whether the conductivity of such portions is finite or infinite

is of no moment in electrostatics. On the other hand, both Ampère's theory of magnetism and Weber's theory of diamagnetism suppose the existence of *perfectly conductive particles*, and are thus strongly supported by our result.

In discussing Weber's theory of diamagnetism, Maxwell \* points out that the currents excited in a perfectly conductive body by any external cause are entirely confined to the surface of the body. Thus the *perfectly conductive bodies* in Theorem I. may be replaced by *perfectly conductive surfaces*, without altering any of our conclusions; but it would be hard to decide whether a perfectly conductive geometrical surface is or is not a physical possibility without knowing more of electromagnetism—not to speak of ordinary matter.

#### 4. THEOREM II.

*In metals, and in other non-electrolytes whose conductivity is finite, the transmission of currents must be effected by the intermittent contact of perfectly conductive particles.*

For if there were not these intermittent contacts, any given two of the conductive particles would be either permanently in contact with one another, or permanently out of contact, and there would be only two cases to consider. If throughout the substance there extended continuous chains of (perfectly) conductive particles in contact with one another, the substance as a whole would be a perfect conductor; while in the absence of such chains of particles, the substance would be a perfect non-conductor. Finite conductivity can only exist when the contacts are intermittent.

#### 5. An immediate corollary is

#### THEOREM III.

*If we suppose that in a substance at the absolute zero of temperature there is no relative motion amongst the molecules or amongst their appreciable parts, it follows that every substance at this temperature must have either infinite specific resistance (which need not imply infinite dielectric strength), or infinite conductivity.*

For the denial of relative motion involves the denial of that intermittence of contact which in Theorem II. was shown to be necessary to finite conductivity.

This conclusion is in accordance with the experiments of

\* 'Electricity and Magnetism,' 2nd ed. vol. ii. § 840.

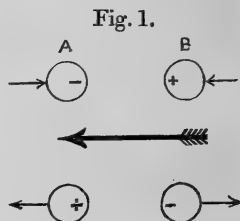
Dewar and Fleming\* on the resistance of pure *unalloyed* metals at very low temperatures. In the case of all the pure metals examined by these authors (platinum, gold, palladium, silver, copper, aluminium, iron, nickel, tin, magnesium, zinc, cadmium, lead, and thallium), the temperature-resistance curves are almost straight lines, and these, being produced, would pass very nearly through the point whose coordinates are zero temperature and zero resistance.

The same was *not* found to hold good for the temperature-resistance curves for alloys; but if these curves could be pursued far enough by experiment, they must be found, I think, to terminate at the origin of coordinates, like those of the pure metals.

## 6. DISSIPATION OF ENERGY IN A CONDUCTOR CONVEYING A CURRENT.

In fig. 1 let A and B be two perfectly conductive particles (whether molecules or parts of the same or of different molecules we need not consider), and let them be approaching one another. Suppose also that there is an applied E.M.F. acting from right to left (as indicated by the large arrow). Then, generally speaking, A will be negatively electrified, owing to a previous encounter with some particle farther to the left, and for a similar reason B will in general be positively electrified. When A and B collide, the usual effect is to leave A on the whole positively electrified, and B negatively electrified.

Remembering that the conductivity of A and B is perfect, let us consider what transformations of energy are effected by movements and collisions of this kind. Before the collision, A being negatively electrified is urged towards the right by the applied E.M.F., while B being positively electrified is urged towards the left: that is, A and B are urged *together*, and are gaining kinetic energy at the expense of the source of applied E.M.F. After the collision, the electrifications are, generally speaking, reversed, so that A and B are now being urged apart by the applied E.M.F., and continue to gain kinetic energy as before. Further, when particles such as A and B come into collision, so as to cause a re-adjustment of their electrifications, and also when they are in motion between two collisions, electromagnetic disturbances will be produced in the intermolecular ether; but since all



\* Phil. Mag. Sept. 1893, p. 271.

the conductive particles are perfectly conductive, no electromagnetic energy can penetrate within them. Thus the energy expended by the source of E.M.F. which maintains a steady current through a conductor is converted partly into additional energy of the molecules, and partly into electromagnetic disturbances of the intervening ether: that is, *the dissipated energy takes the form of heat*, as we know from experiment.

## 7. OHM'S LAW.

In the case of a metal wire (especially one at a bright red heat), Ohm's Law has been verified with great exactitude, the results of the experiments designed by Maxwell and carried out by Chrystal being summed up by the latter in the following words \*:—"If we have a conductor [of iron, platinum, or German silver] whose section is a square centimetre, and whose resistance for infinitely small currents is an ohm, its resistance (provided the temperature is kept the same) is not diminished by so much as the  $1/10^{12}$  part when a current of a farad per second passes through it."

Now when a current is conveyed through a substance by intermittent contacts amongst a number of perfectly conductive particles, the effective conductivity depends firstly on the properties of the intermolecular medium, and secondly on the size, form, distribution, and movements of the particles themselves. In order that the resistance of the conductor may be sensibly constant—in order, that is, that the current transmitted may be sensibly proportional to the impressed E.M.F.—two conditions must evidently be satisfied:—

(i.) For such values of impressed electromotive intensity as exist in the intermolecular spaces (say about .003 volt per cm.) the relation between electromotive intensity and electric displacement must be sensibly linear.

(ii.) The forces which the particles of the substance experience owing to the impressed E.M.F. must be very small in comparison with the ordinary intermolecular forces, so that during the time of a single molecular excursion the motion of no particle is appreciably influenced by the presence of the E.M.F. If we suppose that in the conducting substance we can maintain a steady distribution of temperature which is independent of the current flowing through, this second condition implies that the particles of the substance under the steady distribution may be regarded as a system of perfect conductors, whose coordinates are explicitly given functions of the time, and are sensibly unalterable by an E.M.F.

\* B. A. Report, 1876, p. 61 of Reports.

impressed upon the system from without. This condition, combined with (i.), will evidently give us Ohm's Law.

Now the forces actually present and tending to modify the heat-movements are of two kinds: electromagnetic and electrostatic.

(a) *Electromagnetic Forces*.—The passage of a current through a conductor gives rise to a magnetic field, which may or may not appreciably affect the conductivity. The thin iron wire used by Prof. Chrystal was  $\cdot 0021$  cm. in radius, and the greatest value of the magnetic force due to a current of 1 ampere per square centimetre of cross section would be in absolute measure about  $\cdot 0013$  (at the surface of the wire), the square of the greatest magnetic force being thus about  $\cdot 0000017$ . The average value of (magnetic force)<sup>2</sup> over the cross section of the wire would be half of this, or  $\cdot 00000085$ ; that is, about  $\cdot 0000039$  of the square of the terrestrial "total force" in these parts.

Now Lord Kelvin found\* that the change of resistance due to *transverse* magnetization of an iron plate by a powerful Ruhmkorff electromagnet was only just decided enough to be distinctly appreciated with the apparatus which he employed, and we may therefore conclude that in Prof. Chrystal's iron wire no perceptible change of resistance could have been produced by the magnetic field of the current. In other metals the effect must be still more insignificant.

On the other hand, the *longitudinal* magnetization of an iron wire perceptibly increases its electrical resistance, so that it would be easy to construct a simple conductor whose resistance at a given temperature was a function of the current-strength. For let a flat bobbin be wound with iron wire, so that each turn has the form of an elongated rectangle, and then let a further quantity of iron wire be wound in a similar circuit embracing the first. Finally let the coils be joined in series with a source of E.M.F. When a current is sent through the circuit, each coil will magnetize longitudinally some parts of the wire of the other coil, and so, for a given temperature of the wire, the resistance will increase with the current.

(b) *Electrostatic Forces*.—Let us attempt to calculate the electrostatic energy per cubic centimetre which a mass of iron possesses in virtue of a current flowing through it with a "density" of 1 ampere per cm.<sup>2</sup> To do this we must assume some value for the specific inductive capacity of iron †, and

\* Phil. Trans. 1856, especially pp. 747-749.

† In electrostatic measurements conductors appear to have an infinite specific inductive capacity; but here, where the potential really varies from point to point through the metal, it is the true (finite) specific inductive capacity which concerns us.



in order to take a sufficiently unfavourable view of the question, let us assume the value to be as high as 20. Taking the specific resistance of iron in electromagnetic measure to be 10,000, and remembering that 1 ampere = .1 absolute unit, we have for the electromotive intensity 1000 electromagnetic units of potential per cm., *i.e.*  $1000 \div (3 \times 10^{10})$  electrostatic units per cm. Hence the electrostatic energy per c. c. due to the impressed E.M.F.

$$= \frac{20}{8\pi(3 \times 10^7)^2} \text{ ergs ;}$$

while to calculate the *thermal* energy per c. c. at "a bright red heat"—the temperature of the iron in the British Association experiments—we have:—

Temperature above absolute zero (say)	= 727 + 273
	= 1000 Cent. degrees,
Density of iron . . . . .	= 7.8,
Specific heat . . . . .	= .113,
One gram-water-degree of heat . .	= $42 \times 10^6$ ergs.

Thus (roughly speaking) the thermal energy per c. c. reckoned from absolute zero

$$= 1000 \times 7.8 \times .113 \times 42 \times 10^6 \text{ ergs.}$$

A comparison of these results gives

$$\frac{\text{electrostatic energy due to impressed E.M.F.}}{\text{thermal energy}} = \frac{1}{4 \times 10^{22}}$$

only, even on our assumption that the specific inductive capacity of iron in electrostatic measure is as high as 20. If we suppose that half the thermal energy is potential and half kinetic, then the electrostatic energy would be  $1 \div (2 \times 10^{22})$  of the thermal kinetic energy ; that is, would be equal to the additional energy required to increase the existing velocity of every particle by one part in  $2 \times 10^{22}$ . When due account is taken of these results it is not surprising to find that in iron at a given temperature the specific resistance for a current-density of one ampere per cm.<sup>2</sup> differs from the specific resistance for an infinitesimal current-density by less than one part in  $10^{12}$ .

The same remarks apply with even greater force to platinum and German silver, the other metals examined by Prof. Chrystal, since the *magnetic* influence of the current on the resistances of these metals must be far less than even in the case of iron.

From considerations similar to these, we should expect in all true conducting substances (even in those having marked

magnetic properties) to find a sensibly linear relation connecting current-density with electromotive intensity in the neighbourhood of each point.

### 8. CONTACT E.M.F. AND THE PELTIER EFFECT.

It will now appear that, by assuming in each molecule a mere arrangement of conducting and non-conducting parts, we may realize what is at all events a working model of contact E.M.F. and of the Peltier effect; and even should our model serve no other purpose, it directs our attention to a possibility which seems so far to have been overlooked, and which must, indeed, continue to be overlooked so long as each metal is regarded as homogeneous. As it not my object to state with becoming vagueness an hypothesis as to the nature of Peltier's phenomenon, but rather to picture as clearly as possible a mechanism whose principle may perhaps be suggestive of the truth, I shall assume for the molecules such a structure and distribution as appear most favourable to simplicity of treatment.

Suppose, then, that in one of the metals with which we have to deal, each molecule is of the form indicated in fig. 2: a central perfectly conductive body, charged (say) positively, being completely surrounded by an insulating layer, and this again being partially (though not completely) enclosed by a number of perfectly conductive particles. It will be convenient to suppose that in each molecule these outer particles are all electrically connected with one another. When two such molecules come into collision, the outer particles of the one may not in general be reduced to the same potential as those of the other, for the electrical oscillations occasioned by the contact may not have time to subside into insignificance before the encounter is ended. But the general tendency of a collision between two molecules will be towards an equalization of the potentials of the outer particles, and the average values of potentials and charges amongst any considerable number of molecules will be the same as if, during each molecular encounter, this equalization has been completely effected.

Fig. 2.



It will here be convenient to introduce the term "conduction-potential," and as we proceed the following definitions will be found useful:—

*The conduction-potential of a molecule* is the potential (or average potential) of its outer conductive particles.

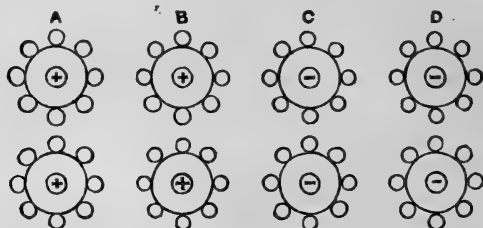
*The conduction-potential at a point* within a metallic body is the average conduction-potential of the molecules in the neighbourhood of that point.

Let us now turn to the case of a considerable mass of metal, made up entirely of such molecules as that sketched in fig. 2; every molecule having the same structure and the same internal charge. Let us suppose also that the mass of metal is at the same temperature and in the same physical condition throughout, so that the average distance between adjacent molecules is the same in the neighbourhood of each point. If the metallic body is subjected to electrostatic induction, it is easy to see that no electric influence from without can penetrate far beyond the surface; for the outer particles of the superficial molecules, owing to their intermittent contacts with one another, will screen the interior of the metal as a network of continuous wires might do, and at a depth of a very few molecules beneath the surface the screening will be practically complete. Thus any charge communicated to the conductor will be confined entirely to the superficial layers of molecules; and it follows that if between any two points well within the metal there were a difference of average conduction-potential, there would be a general flow of electrification from the higher towards the lower potential. The average conduction-potential within the metal does not therefore vary from point to point, and account being taken of the equality of the internal charges of the molecules, it follows that the average potential of the intermolecular ether is similarly free from variation. This implies that the total electrification of any considerable assemblage of molecules within the metal is sensibly zero; so that the average charge on the outer conductive particles of each molecule is equal and opposite to the fixed charge on the central particle. The conclusions of this paragraph have been necessarily confined to molecules not too near the surface; for although the general tendency of an encounter between two molecules is always to equalize their conduction-potentials, these potentials change somewhat after the molecules have become separated, and near the free surface of the body the change will be systematically greater for the molecule which moves outwards after collision than for that which moves inwards.

We may now try to realize what will happen when contact takes place between two metals whose molecules are constructed on the general plan of fig. 2, while those of the one metal are not identical with those of the other. The most simple and intelligible view will be obtained by supposing the molecule of the one metal to have a positively charged central particle, while the molecule of the other has its central particle negatively charged (fig. 3). Consider what would

occur if we could start from a condition in which each of the *border* molecules, A, B, C, D, &c., had *on the whole* no charge; a condition, that is, in which the outer particles of each molecule had a charge equal and opposite to the fixed charge

Fig. 3.



of the central particle. (We have already seen that this is true for the *average* molecule *within* a homogeneous metallic mass.) Now when B and C come into collision, it is evident that the outer particles of B will lose some of their negative electrification, while the outer particles of C will lose some of their positive; and thus we see that when the distribution of conduction-potential has become steady, such border particles as B or C will have on their outer particles a (negative or positive) charge *less* than the (positive or negative) fixed central charge, and to a smaller extent the same will be true of particles (such as A, D, &c.) more remote from the border. But when the settled condition has been reached, the passage (say) of B backwards and forwards between A and C will not change the distribution of charges amongst the molecules; and the condition that no change of the kind shall take place is that when two molecules are in a position to collide their conduction-potentials shall be equal. Now when B approaches C (which has on the whole a negative charge) its potential is lowered, and when B returns towards A its potential rises again, so that if B in its backward and forward motion is not to act as a systematic carrier of electrification between A and C, the conduction-potential of A must be higher than that of C. Similarly, by considering C as moving backwards and forwards between B and D, we can see that B must have a higher conduction-potential than D.

This gives us a *contact-difference of conduction-potential*.

If we suppose our analysis to become a trifle less penetrating, such molecules as B (and to a less extent A, &c.) will appear to be positively electrified, C, D, &c. will appear to be negatively electrified, and molecules farther removed from the border will appear unelectrified. With still less micro-

scopical vision, we shall find the conduction-potential constant from point to point throughout the mass of metal on either side of the surface of separation; but as we approach that surface from the left, the conduction-potential begins to diminish, changing very rapidly by a finite amount as we pass through the boundary.

We now come to a theorem which is certainly true for our model, and which seems to me as certainly true for any mechanism which could be devised to represent the Peltier effect; but for the sake of avoiding questions of too controversial a character, the statement may be made in this conditional form:

#### THEOREM IV.

*In our model, the contact-difference of conduction-potential between two metals is equal to the coefficient of the Peltier effect.*

For when a molecule at the junction is moving backwards and forwards between places of different potentials, provided no current flows through the junction, as much electrification is carried from the lower to the higher potential as from the higher to the lower, and on the whole there is no transformation of electric energy into heat, or *vice versa*. But when a current flows across the junction from the metal of lower to that of higher conduction-potential, the molecules at the junction are persistently carrying more electrification from the lower to the higher potential than they bring back with them on their return, and thus on the whole the movements of the molecules at the junction are systematically opposed by electrostatic forces. It is evident from elementary considerations that the quantity of electricity which has crossed the junction, multiplied by the step of (conduction-) potential up which it has passed, is the measure of the total work done by the molecules against electrostatic forces, and is therefore the measure of the heat absorbed. Similarly, when a current has been flowing from the metal of higher to that of lower conduction-potential, the quantity of electricity which has crossed the junction, multiplied by the (negative) step of conduction-potential, is the measure of the (negative) heat absorbed; that is, numerically, of the heat given out. Hence, in our model, the coefficient of the Peltier effect is equal to the contact-difference of conduction-potential.

Again, generally speaking, we may expect a difference of conduction-potential between a hotter and a colder portion of the same metal, owing to the increase of molecular distances which rise of temperature produces; and it is evident that (*on our model*) the specific heat of electricity for any metal is equal to the rise of conduction-potential for one degree rise of temperature.

9. From these results we pass on to

### THEOREM V.

*For any pair of metals at the absolute zero of temperature, the Peltier effect vanishes.*

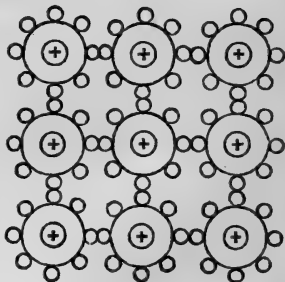
This is evidently true for our model, for when the molecules are all reduced to relative rest, and there is permanent instead of intermittent contact amongst their outer particles, the conduction-potential will be uniform throughout both metals, and at the junction there will be no Peltier effect. But whatever view we take of the nature of the phenomenon, the proposition is necessarily true. For if the Peltier effect had a finite value for a pair of metals at the absolute zero of temperature, we could cause an absorption of heat by sending a current through the junction in the proper direction; and this is impossible, since there is no heat to be absorbed.

### 10. VOLTA E.M.F.'s.

We must now consider a possibility suggested by our model, and referred to in the opening sentence of §8. It is not difficult to see that, with molecules constructed on the plan of fig. 2, even when all measurements are made *in vacuo*, the conduction-potential of a mass of metal is not in general the same as the potential estimated by work done on an external charged body, or by electrification induced on a second mass of metal insulated from the first,—potential measured in the latter way being called for distinction the *induction-potential*.

We may realize this most easily by considering the case of two metals in contact at the absolute zero of temperature, for then, in accordance with the last section, the Peltier effect at the junction vanishes, and the *conduction-potential* is the same throughout both metals; while on the other hand the difference of *induction-potential* may be finite. Let fig. 4 represent diagrammatically a very large number of molecules which are at rest with their outer conductive particles in electrical contact throughout. Let the fixed central charge of each molecule be positive. Then, if the outer conductive particles of each molecule formed a complete envelope around the central charge, the *induction-potential* of the metal would be identical with its *conduction-potential*, and the same as if the fixed central charges did

Fig. 4.



not exist. But since we suppose the fixed charge in each molecule to be *incompletely* screened by the outer particles, it follows that at external points in the immediate neighbourhood of the metallic body the potential is raised above the conduction-potential by the fixed central charges. If these last were negative instead of positive, the potential just outside the metallic mass would be lower than the conduction-potential; and we may suppose that at any given temperature (such as the absolute zero with which we are dealing) the difference between the conduction-potential of a metallic body and the potential just outside the body depends upon the nature of the metal. Thus, even *in vacuo*, if two metals at the absolute zero of temperature be connected together so as to have the same conduction-potential, their induction-potentials may be different; and in general, whatever the temperature of the metals in contact, we may expect an inequality between difference of *conduction-potential* and the difference of *induction-potential*.

Before attempting to devise a model of Peltier's phenomenon and of electromotive forces of contact, I had held the opinion—in common, I believe, with the majority of disputants in the contact-force controversy—that the inductive measurement of potential-differences in a sufficiently perfect vacuum must conclusively decide the points at issue. But if in reality there should be, as the model suggests, a difference between conduction-potentials and induction-potentials, we must not rely upon inductive experiments, even in a perfect vacuum, to determine the seats of electromotive force in a voltaic cell. For when we are dealing with the flow of currents through metals, it is the *conduction-potential* which concerns us.

## 11. THE TRANSPARENCY OF METALS.

A difficulty in connexion with this subject is stated by Maxwell in the following well-known passage\* :—"Gold, silver, and platinum are good conductors, and yet, when formed into very thin plates, they allow light to pass through them. From experiments which I have made on a piece of gold-leaf, the resistance of which was determined by Mr. Hockin, it appears that its transparency is very much greater than is consistent with our theory, unless we suppose that there is less loss of energy when the electromotive forces are reversed for every semi-vibration of light than when they act

\* 'Electricity and Magnetism,' 2nd ed. vol. ii. § 800. Wien (Wiedemann's *Annalen*, xxxv. pp. 41-62) found a silver film to have only such an opacity as would be deduced from about 1/440 of its actual conductivity.

for sensible times, as in our ordinary experiments." Now we have seen that conduction is not a perfectly continuous phenomenon, but is due to innumerable encounters among perfectly conductive particles, and without entering upon any calculations (which indeed would be a difficult matter) we can see that there are, broadly speaking, two reasons why the opacity of metals is so much smaller than is indicated by Maxwell's analysis: these are, heterogeneity of structure and intermittence of contact.

To realize the influence of heterogeneity of structure without the complication of intermittent contacts, take the case of a metal at the absolute zero of temperature. We have then virtually to deal with a network of perfect conductors, constituting a body which as a whole has perfect conductivity, and of which even an excessively thin film would be an effectual barrier to electromagnetic waves, provided that the wave-length were great enough to justify us in treating the metal as homogeneous. But if we consider an extreme case, where the wave-length of the disturbance is negligible in comparison with the dimensions of a single conductive particle, a very thin layer of the metal will be far from absolutely opaque. For the conditions of the problem will then be the same as if we had ordinary luminous radiations obstructed by an agglomeration of perfectly reflecting bodies of appreciable size. Of course these extreme conditions are not realized in the case of the light transmitted by a metallic film; but if we may suppose that the diameter of a conductive particle is not quite negligible in comparison with a wave-length of light, it is clearly to be expected that very thin layers of the metal will fall short of that absolute opacity which in this case would follow from the assumption of homogeneity.

When we pass to the consideration of metals at ordinary temperatures, the conductivity for steady currents is finite; but for electromagnetic waves of short period we cannot even treat the metal as an agglomeration of finitely conductive particles continuously in contact with one another. It is evident that the shorter we make the period of the electromagnetic disturbance in comparison with the average intercollisionary period of a (perfectly) conductive particle, the more nearly do the particles act as if permanently insulated from one another, and the less efficiently does the metal perform the functions of an electromagnetic screen.

Further considerations might be added concerning the average interchange of electrification between colliding particles when the electromotive intensity tending to produce such interchange is very rapidly alternating; but enough has



been said to show that the opacity of conductors must be far less for luminous radiations than for electromagnetic disturbances of long period, and we may fairly expect, I think, that the transparency of metals is to be explained without attributing any new properties to the electromagnetic field.

The second part of this paper will deal with electrolytic conduction and disruptive discharge.

*Note added April 30th.*

In the course of the discussion Prof. S. P. Thompson objected to the arrangement of molecules in rectangular order, and he further suggested that the arguments might only be applicable in two dimensions. I had omitted to mention that the figures were intended to be sectional views of three-dimensional models, while the rectangular arrangement of molecules was merely adopted to save prolixity in the descriptions, and was so far from being essential to the investigation that the case of irregularly distributed coordinates and velocities was constantly before my mind. Another point raised by Prof. Thompson must also be considered here: in § 6 it does not necessarily follow that two conductive particles oppositely charged like A and B (fig. 1), approaching one another and subject to the influence of an external E.M.F. acting from right to left, would have the signs of their respective electrifications reversed by a *momentary* contact; in some encounters the readjustment of electrifications might even be in the opposite sense; but I think we may safely admit that *in the long run* the effect of innumerable collisions amongst such conducting particles as A and B will be to transfer electrification in the direction of the impressed E.M.F.

Prof. Rücker recalled a difficulty, which Lord Kelvin pointed out some time ago, in connexion with the collisions between molecules. If we suppose the molecules to be constituted like little pieces of elastic solid, every collision will cause some additional amount of translational energy to be converted into energy of vibration, and heat-energy will be continually running down into energy of shriller and shriller vibrations, that is, into energy of a lower form. In the foregoing pages, electrical contact between particles is supposed to occur during a collision, and Prof. Rücker remarked that the method suggested for avoiding an electromagnetic degradation of energy left untouched the corresponding mechanical difficulty. I have made some attempt to deal with this

mechanical question in a previous paper\*, where it was shown (§§ 10, 11) that, granted the fundamental assumption and an infinite propagation-velocity for gravitational stress, we may construct an atom having a finite number of freedoms. But in whatever way mechanical degradation of energy were eliminated, the difficulty of electromagnetic degradation would also have to be met, and without the doctrine laid down in Theorem I. there appeared to me to be no means of escape. Without making any assumption as to the constitution of a molecule or the nature of a collision, we may admit that in any body not absolutely cold there are particles in relative motion, so that two neighbouring particles are sometimes nearer together and sometimes farther apart. To realize the intermittence of contact required by Theorem II., we have only to suppose that when (but not until) the proximity of two particles has reached a certain limit electrification is capable of passing freely from one to the other.

The question of perfect or imperfect conductivity in the ultimate particles of bodies must be of importance in relation to the constitution of matter and its connexion with the ether ; and whether or not the demonstrations above can be generally accepted as conclusive, the subject is certainly one which will repay further investigation.

### V. *Some Observations on Diffraction.*

*By* W. B. CROFT, *M.A.*†

[Plates I.-IV.]

**I**T is proposed to illustrate various forms of this phenomenon by photographs‡ produced directly from the wave-interference.

After the inauguration of the idea about 1665 by Grimaldi, Hooke, and Huygens, there was little progress, either in extended observation or in philosophical grasp of the principles, until the beginning of this century. Since that time the subject has been treated in two ways.

#### 1st. *The Diffraction of Fraunhofer and Schwerd.*

This kind is familiar to many through the observations of Sir John Herschel of Diffraction in a Telescope. It is sometimes described as the Diffraction from Parallel Light.

\* "A Theory concerning the Constitution of Matter," *Phil. Mag.* February 1892, p. 191.

† Communicated by the Physical Society: read January 26, 1894.

‡ It is not convenient to reproduce all the photographs: the selected figures 2, 3, 4, 10, 12, 13, 71, 72, 75, 83 will be found on Plates I.-IV.

Although more often named after Fraunhofer, as is due to the first great worker in this direction, high tribute is always paid to the more perfect consummation of theory and experiment which was published by Schwerd of Spires in 1835.

A telescope is focussed to a star or a distant point of light, and various limiting apertures are placed on the outer side of the object-glass. Consider, first, the case of two or three narrow parallel lines of light : they constitute an elementary grating, and light from the star passing from them to the object-glass will come as if from several stars lying on either side of the real star, all being spectral images except the central one. The object-glass focusses these at the usual place, then the eyepiece magnifies them and transmits parallel rays of light ; so there is a broken line of light across the field, consisting of the plain image at the centre and the spectra of the successive orders on either side. More complex limiting apertures give these radial groups of images of the source of light, of which the number and direction are regulated by the general form of the aperture : thus a triangle will give three lines across the field or a six-rayed star, a square will give a four-rayed star ; a circle concentric with the object-glass, however, will give concentric circular spectra.

The objects whose effects have been photographed consist of combinations of thin circular lines of light on a dark glass plate  $\frac{3}{4}$  inch diameter ; this fits into a cap at the end of a telescope, and each figure in turn is brought to a small opening in front of the centre of the object-glass : this is known as Bridge's apparatus, constructed some years back for this form of diffraction. Fig. 8 almost represents these figures ; it has slight traces of diffraction of the other kind. Figs. 1-7 (figs. 2, 3, 4 on Pl. I.) represent the Fraunhofer diffraction of the seven more complex figures : the simplest figure, which consists of two concentric circles, gives concentric spectra by both methods of observation.

## 2nd. *The Diffraction in Shadows : Fresnel's Diffraction.*

This is described by Lord Rayleigh as the Diffraction when the source of light is not in focus, or in Jamin's *Cours de Physique* as Diffraction from a Spherical Wave. Light is condensed on a minute pinhole in a thin metal plate ; about a foot from this the diffracting object is placed, and at a similar distance beyond a microscope eyepiece receives the shadows : they may be observed with the eye or projected on the screen of a camera for photography. The rays emerge from the eyepiece parallel, and give an image on the screen which varies in size but not in quality as the screen is moved ;

infinite changes, however, are made by variations in the relative distances of the source of light, object, and lens or eyepiece.

In order to consider a fundamental principle of importance, take at first more simple apparatus, a convex lens instead of the Huygens eyepiece, and let the object, which is the glass plate with circle combinations, be illuminated with parallel uncondensed sunlight. If the lens is placed at its focal distance from the object, rays emerge parallel and make simple images of circles without any diffraction developments; they are always in focus wherever the screen is placed, and are naturally greater when it is more distant. If the lens is slightly moved from this position in either direction, the emerging rays cross one another and produce interference developments. The figures made when the lens is moved towards the object are inferior in definiteness.

A wave impinging on an edge gives rise to the secondary waves of Huygens, and from each new centre waves spread out in all directions, although the incident light may have a plane front or be a parallel pencil; but a pencil, after emerging parallel from a lens, cannot be considered to have rays striking out obliquely so as to interfere. From this may be imagined the formation of diffraction-rings in a telescope directed to a star when the eyepiece is moved so that the image made by the field-glass is out of its focus; the image is nearly a point of light; while the rays emerged from the eyepiece parallel they would not interfere, but directly they cross one another on emergence they give rise to systems of concentric rings. This phenomenon may be well seen by looking through the eyelashes towards a distant lamp while a fine rain is falling: minute spheres of water fall upon the eyelashes; these short-focus lenses make images of the lamp in front of the eye, and the lens of the eye cannot focus or turn parallel the rays from these points; for a moment a number of fine concentric rings may be seen, which are constantly evanescent and constantly renewed by fresh-falling specks of water.

There is another phenomenon sometimes revealed when a divergent pencil from a short-focus lens or spherical reflecting surface falls upon the eye in such a way that the eye cannot focus it: a small illuminated disk is seen with fine ramified lines from the centre; in this the eye sees its own blood-vessels: this is easily seen by holding a pinhole near to the eye.

Abundant examples of diffraction may be observed without any apparatus: a distant lamp viewed through the eyelashes on a dry evening appears with many spectral images made by this simple grating: an umbrella can be seen in the same way

to act as a rectangular grating. If the eyelids are adjusted to the lamplight, 8 or 10 horizontal exterior bands will easily be produced. Most plate-glass windows have become gratings through the scratching by repeated cleaning.

To return to the main experiment. Stronger effects are produced, of course, when sunlight is condensed on to the pinhole, and in this case the position of the convex lens for giving parallel rays on emergence, or for giving the plain image of the object without diffraction, is not exactly its focal distance from the object, for the divergence of the incident rays has some influence; but there always is such a position. Moreover, the elementary experiment cannot be made with the Huygens eyepiece which is now used, for it has not an external focus. Fig. 8 shows the result of placing the object close up to the eyepiece; the beginnings of diffraction may be seen. Fig. 10 (Pl. I.) shows further developments when the distance is increased, and figs. 9, 11, and 12, 13 (Pl. II.) give the best effects I have at present been able to produce. In these and in most of the other figures a magnifying-glass is necessary to reveal all the fine detail made by the crossing waves in the shadows. It is clear that if the object is capable of giving spectra passing out with much obliquity, they can never come into the field of the eyepiece by this method of observation; and the eyepiece can never focus them, as it does in the Fraunhofer method, in which case the field-glass brings them to the focus of the eyepiece.

It may be said that the Fraunhofer diffraction gives numerous images of the source of light set in radiating forms which depend on the shape of the object, while that of Fresnel commonly gives the main shape of the object embellished with fine detail in the spaces between its various parts, and sometimes curiously inverted in its leading features.

A simpler form of this arrangement demonstrates a leading idea in wave theory: parallel sunlight falls upon a convex lens, while the diffracting object is between this and the screen of the camera, which has no lens. Fair diffraction-effects are made when the object lies in the converging rays, and they are better when it is moved to the divergent pencil, but when it is at the focus the plain original figure is reproduced. At the focus the several rays that started from one point of the sun have again all reunited; so that in passing the object, although there are many separate rays, there are no two rays which came from the same original point; and it is only such as these which can produce interference. Here may be seen, in a certain sense, an object and real image on the same side of a convex lens.

*Diffraction in a Microscope.*

Some notice of this important part of the subject is necessary, although it may not be supported by much illustration or experiment.

It is well, first of all, to be clear as to compound pencils of light which are more or less on the same axes. In a straight line lie A, B, C, D, E, a candle, a device in wire, a convex lens, the images of the candle and the wire : here are two pencils much intermingled : A is in focus at D, but the light here is also impregnated with the shadows of B, which are indefinite and unfocussed, covering a larger area than when focussed at E ; and at this point there is also the indefinite unfocussed light of A.

Very often the object on the stage of a microscope diffuses the illumination and becomes a new source of light, and there is no need to consider pencils from the original source of light. But here we will take the case of a microscope with a diffraction-grating on the stage and a small opening in the diaphragm below. Light passes on to the objective from the grating as if from several small apertures ranged side by side, in pairs of corresponding spectra on either side of the central point, which is white. The objective makes images of these just above itself, and one image of the grating farther on at the top of the tube. If the eyepiece is removed, the eye is able to focus the rays diverging from these images and to see them clearly. But the eyepiece when in its place could not focus such diverging pencils : their light spreads out and fills the field of the eyepiece with general illumination. The visibility of the detail of a finely divided object depends upon shadows thrown by oblique rays. In the case of a grating these oblique rays are so definitely arranged that they go either to the first, second, or higher spectra, and to nothing between. The central pencil comes through the grating normally in parallel rays, and carries with it no appreciable impression of the detail ; experiment shows that on placing a stop above the object-glass to cut off the spectral images, the lines of the grating can no longer be seen, although there is still good illumination. Now the first lot of oblique rays, while on their way from the grating to its focus in the eyepiece, take their course through the first spectra ; but they are unfocussed as regards the grating at that position just above the objective, covering a larger area than the spectra. In theory perhaps it is conceivable that by stopping out the spectra alone, and not this larger area, there might be a balance of rays which would betray the shadows at the eye-

piece. In practice, however, the first spectra are necessary, and perhaps often sufficient, to show the detail: sometimes the higher spectra may be needed to add breadth to the shadows. In fact, from ordinary objects rays of all degrees of obliquity are available to mark the shadows, but from objects capable of diffraction there is no degree of obliquity less than that which tends towards the first spectrum, and the aperture of the objective must not be too narrow to receive these rays.

The question naturally arises, how far it is possible to know whether an image is a reproduction of the general form of the original object or a diffraction modification: so far as my experience goes, the two appearances may be distinguished. Of course in perfect theory, even if an image could be saved from spherical and chromatic aberration, it must suffer something from the waves: the image of a star in a telescope must be enlarged on this account; but there is a great difference between this falsification and that which arises when the eyepiece is taken out of focus. Fig. 82 is a species of the diatom *Triceratium favus*: it appears as a spotted framework of ill-defined outlines with little groups in the spaces; but the microscope can be adjusted so as to show a well-defined honeycomb with clear hexagonal spaces. In an experiment described above, figures known to be circles are reproduced in their own true form when at one position with regard to a convex lens, and more elaborate ill-focussed forms at positions on either side of the former: it is reasonable, then, to apply this test to distinguish between several images of an unknown original. No doubt the simpler form, which is taken to be the true one, might often be resolved into something more complex by a stronger objective, but this one in its new conditions would again be simple and well-defined amidst its possible diffraction derivatives.

I have not sufficient familiarity with the use of the highest microscope powers, and can imagine that the foregoing tests are not easy, if indeed possible, to apply in such cases; but I suppose that with  $\frac{1}{4}$ -inch and lower powers there is no need for uncertainty as to the practical form of the original object.

#### Fresnel's *Diffraction from Geometrical Figures.*

Some interesting details can be observed from the shadows about other figures of Bridge's series. It may be here noted that such objects may be made by drawing rather thick figures in ink upon a card about 1 foot square and reducing by photography to 1 inch square: the negatives so produced give the desired transparent lines on a dark ground: it will be understood that a circle means a circular line of light in

distinction to a circular area. The play of light-waves in a shadow gives rise to infinite paradox. The most notorious is Arago's bright spot at the centre of the shadow of a circular disk, with which he astonished Napoleon Buonaparte: squares and triangles turn about and point inwards: needles seem to be split down with the light and the two parts point outwards, the thinner needle having the broader central cleft: lastly, lines inclined to one another have the effect of resolving one another into transverse flakes.

Simple figures may be drawn to give a partial explanation of these curious results.

Fig. a.

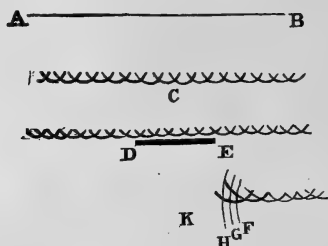


Fig. a illustrates the ordinary principle of Huygens, that a wave-front, AB, goes on as a similar wave-front, C, if it be supposed that each point gives rise to a secondary wave: when this strikes upon an obstacle, DE, the waves at the edge, being isolated and not supported by similar waves on the one side, may pass forward so that in directions F, G, H one is always  $\frac{1}{2}$ ,  $\frac{3}{2}$ ,  $\frac{5}{2}$  of a wave-length in front of the other, causing interference or darkness: these are the exterior shadows: also there can be imagined the action of waves from D and E about a position K which gives the interior bands.

Fig. b.

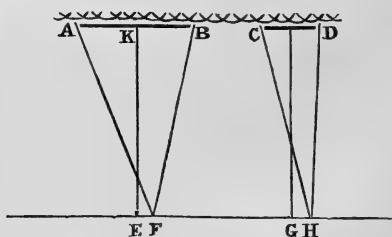


Fig. b shows that waves from A and B must always reach E in the same phase, so at the centre there is always light; at F,



if the difference of  $AF$  and  $BF = \frac{\lambda}{2}$ , there will be darkness. Now if  $CH$  and  $DH$  are more nearly parallel than  $AF$  and  $BF$  are, then, in order to have  $CH - DH = \frac{\lambda}{2}$ , the point  $H$  must be farther from  $G$  than  $F$  was from  $E$ , so the smaller obstacle  $CD$  gives the larger bright centre to its shadow. This principle has many consequences: the thinner needle has the broader bright central line, or as a needle is narrowing towards its point the central line will be opening out: at the corner of a square or triangle there will be wedges of light pointing inwards. The enlargement of the image of a star at the focus of a telescope through diffraction is less in a telescope of large aperture, because the waves from the borders of the lens reach the focus at a greater inclination to one another. Again, the length of a wave of yellow light is about 24 millionths of an inch; if the waves from  $A$  and  $B$  move straight towards one another at  $K$ , then the diameter of the bright spot here will be something less than  $\cdot 000024$  inch, too small to be seen, from which it appears that the condition for making visible these phenomena which are connected with such minute quantities is that  $AF$ ,  $BF$  must be nearly parallel: the object must be narrow, or the screen for receiving the shadow must be distant.

The following notes describe the original figures from which the photographs are the shadows:—

14. A circle with four triangular areas.
15. A circular area with four inscribed dark circles.
16. Four circles touching one another; the lines of the circles are gradually made thinner towards the inner part, but they are complete circles.
19. Two ellipses, each through the focus of the other: Arago's spot at the common part.
20. Three pentagons with a small pentagonal area at the common centre.
- 24 and 29. A square with four external squares at the corners: the latter is the shadow taken at a greater distance from the object; it is covered with fine interference detail.
- 25 and 28. A square with inscribed square and diagonals.
- 23, 26, 27, 30. Right-angled triangles put together in sets of four at an acute angle: the detail contains a number of round spots.
- 31, 39, 40. A chessboard in various states: here again systems of spots are developed.
33. Rows of equilateral triangles, set alternately in successive rows: spots again.

35. Three equilateral triangles with a small triangular area at the common centre.

41. Ten semicircles near to one another and parallel : the feature of this is the broken shaggy brushes at the ends of the semicircles.

43, 44, 45. A parabola lying within another one of smaller parameter ; the lines of light being rather thicker about the vertices. In 44 each vertex has opened, turned the broken edge back and taken a small ball into the open mouth : the bands about the axis, which is not drawn in the original, are diffraction creations : the inner parabola is broken into flakes about the vertex by dark cross lines.

42. An hyperbola and its conjugate, twice repeated, without asymptotes. The flaking appearance is noticeable.

46. Two ellipses, side by side : as a larger circle gives a smaller central spot, the curve at the end of the minor axes gives a smaller spot, and that at the end of the major ones a larger spot : the result is the broadening white line in the figure.

47. Five diminishing circles with internal contact, where the lines are made thinner : here are the shaggy offshoots similar to those in 41.

50. Three circles, near, not quite touching. Arago spots and flaking.

48, 49, 51. Arago spots made by small arcs of circles.

52. A square divided into 4 small squares, in each of these a circle inscribed, not quite touching. Not to mention the small detail, this figure suffers the curious inversion of appearing as 4 circles with inscribed squares.

53. Four circles.

54. A square with an external semicircle on each side.

55. Five small circles in a ring touching one another.

56. Two circles, each through the centre of the other.

57. Two unequal circles, near, not quite touching : the larger spot in the smaller circle, and the flaking disturbance of the larger by the neighbourhood of the smaller.

60, 66. Eight small circles in a ring touching one another : in each case there is the bright spot at the centre of each circle, in 66 there is one at the centre of the whole figure : the formation of the common tangents at the points of contact is not difficult to imagine.

58, 59. The square and triangle which have turned about and point inwards : their sides have been resolved entirely into transverse flakes.

62. A square with thicker lines of light.

61. Not quite a square, a bright square area with an inscribed dark circular area.

65. A pentagon: here, as in several of the figures just above, there is a bright spot at the centre.

*Fresnel's Diffraction from Simple Objects.*

67. The inner part shows Fresnel's interference-lines from a bi-prism, with Grimaldi's fringes at the sides.

68, 69. Narrow slits; 68, with the broader bands, is from the narrower slit. Both slits are so narrow that the exterior bands, through interference of parts of the same wave from one side, do not come in: the bands are given by waves from the two edges. It may be remarked that in exterior bands there is more indication of colour than in interior bands: the neighbouring rays which form exterior bands can travel almost parallel and make coarser bands with more chromatic dispersion. In the case of light passing on to an aperture, care is sometimes necessary to note which of the two effects is predominant.

70, 81. The eye of a bodkin, one to show interior bands, the other to show the exterior bands: it is not easy to develop both effects at once. The bands within the eye are not interference of waves from the two sides, but the exterior bands of each side: it happens that the breadth is such that a band from one side is superposed on one from the other, so the central line is dark.

79. Four round holes of increasing size. This is a case of exterior bands in the bright spaces; the centre of the space may be white or not according to the breadth of the hole: also the rings and spots are brightly coloured. These holes varied from  $\frac{1}{2}$  to 2 millim. diameter. If a hole be taken  $\frac{1}{3}$  millim. diameter, the phenomenon changes and becomes analogous to 68 and 69: concentric spectra are formed in the shadow, and there are no rings in the projection of the aperture.

71, 72 (Pl. III.). The points and eyes of ordinary needles: the one with the broadest central line is the shadow of the smallest needle which is made: here the interior and exterior bands both appear.

80. A quartz fibre about .0005 inch diameter.

73. Wire gauze: each wire gives in shadow 6 dark bands: the spaces give sometimes 2, sometimes 3 bands, showing an inequality of distance. These bands are the exterior bands from the sides of the wire, and give bright colours. The general appearance to the eye is that of a Scotch tartan.

77, 78. Perforated zinc. The former is developed to show the rings in the spaces; these are coloured, and the centre may be white or not according to the size of the holes or their distance from the screen. The latter figure is developed to show the interior bands on the dark parts; they naturally give hexagonal systems. This may illustrate the markings in *Pleurosigma angulatum*, which are regarded as diffraction-bands made by the rows of white spots that form the real structure of the diatom; but, in truth, this case can be realized without the aid of diffraction. Where there are such rows of spots, there must be the lines of shadow between them. The narrowest dark space marked over with diffraction lines has two dark bars separated by a bright central line.

74. Arago's experiment.—The shadow of a threepenny-piece, showing the bright centre. Here parallel sunlight was thrown uncondensed on to the pinhole. The coin was about 18 feet from this, held by a thin wire, and the screen of the camera 18 feet beyond, without any lens. The illumination was not uniform, so that the exterior rings are partly seen: if a lens is used, several rings may be seen around the bright centre, but the complete shadow is too large for the field of view. According to Verdet, Arago employed a circular disk 2 mm. in diameter.

75, 76. Arago's experiment.—Shot fixed on glass; 3 millim., 2 millim., 1 millim. diameter. These were taken with the eyepiece and the ordinary arrangement. In theory there are concentric rings over the whole shadow, but they are more difficult to see than the bright centre. They appear in fig. 76, and in a strong light may be produced with the larger shot. It should be noticed in fig. 75 (Pl. IV.) and fig. 76 how large a bright centre has been made in several places by specks of dust.

Both with the shot and the threepenny-piece, when they are most accurately arranged, as evidenced by the regularity of the rings, a faint dark spot may be seen at the centre of the white spot, and in some positions of the disk relatively to the eyepiece this opens out into a faint dark ring. At present, I have not been able to ascribe with certainty a reason for this secondary effect, but I think it arises because the source of light is not a mathematical point.

83 (Pl. IV.). Conical refraction; external. In conclusion, I venture to pass the strict limits of the subject by showing the crowning triumph of the hypothesis of wave-propagation. Light through 5 minute pinholes passing in a special direction through a crystal of arragonite emerges in 5 cones of light:

the four outer circles show by their imperfection the development of the circle from the two points that are formed by a double-refracting crystal.

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VI. *On some Experiments with Carbon Dioxide in the Solid State.* By Dr. L. BLEEKRODE\*.

WHEN working of late with very low temperatures produced by evaporating solid carbon dioxide I met with some facts which are perhaps not generally known, and may I think prove useful for lecture experiments.

I obtained the solid substance in the usual way from its liquid state, now so easily to be had in large quantities in the iron bottles prepared for industrial purposes. If a cloth bag (first used by Bianchi in 1870) is tied to the delivery-valve, the solid may be readily collected inside, and this method is as effective and more simple than the use of ebonite or metal boxes, which are liable to have their parts frozen together and then cannot be quickly emptied.

*Compressed Carbon Dioxide.*—This substance on being removed from the bag presents itself in a very divided state and therefore evaporates comparatively quickly; but on submitting it in suitable moulds of wood or metal to high pressure, either by hammering, or still better with screw and lever (as for instance the arrangement for regelation experiments with ice), a most compact substance is obtained, in the form of cylinders, disks, lenses, cups, &c. that can much longer endure the heating-effect of surrounding air.

Such compressed cylinders were described by Prof. Landolt in 1884†; he obtained them by hammering the mass together; the specific gravity of the carbon dioxide in that condition was determined, first by calculating the volume of the cylinder from the geometrical dimensions, and

\* Communicated by the Author.

† Landolt, *Chemische Berichte*, 1884, xvii. p. 309.

then by ascertaining its weight with the balance, taking care to collect the gas, which evaporated during the process, in a potash solution, connected with a delivery-tube to the vessel containing the solid substance, the whole arrangement of course standing on one of the scales of the balance. In this way the specific gravity was found to be 1.2 (in the liquid state, at  $12^{\circ}5$  C. it is 0.88), and accordingly the larger pieces of the dioxide sink in water; the smaller ones remaining suspended on the surface owing to the evolving gas. I myself found in different experiments the number 1.3, and even 1.6; this greatly depending on the pressure exerted, which, with my apparatus, could be made very high; at the latter density, the cylinders looked semi-transparent. The great advantage now gained lies in the very slow evaporation. Landolt mentions that he was able to keep a cylinder with dimensions of 25 mm. and 26.8 mm., having a weight of 15.63 grammes, during one hour and a half; I could maintain one, at a temperature of the atmosphere of  $15^{\circ}$  C., having a weight of 41 grammes, during nearly the same time; but he was even able to keep a cylinder of 41 mm. diameter and 53 mm. high during five hours. The surface, as is to be expected, soon becomes covered with ice needles that are easily nipped off, but Landolt is of opinion that a hydrate is also formed.

*Production of Electricity.*—It has been remarked by more than one observer that a strong jet of carbon dioxide, obtained from its liquid, on expanding in the atmosphere, may produce an electric charge of marked intensity. Riess in his well-known book on frictional electricity mentions that, as long ago as 1852, Joly saw electric sparks given off by an iron bottle which was filled with liquefied gas; and also Ducretet at Paris made a communication in 1884, on the appearance of sparks, when he caused the gas to escape from its liquefied state in a box of ebonite, in order to collect the solid substance. More recently Hausknecht\* published the same observation, but adds the important remark that it is necessary, when powerful effects are aimed at, to use a gas absolutely free from air, and therefore that prepared by chemical means is better suited for these experiments than that obtained from natural sources, as manufactured on the Rhine. The cloth collecting-bags show an intense electric charge, emitting a violet light inside, and he got sparks of even 20 centim.; but they do not appear before a dense layer of crust of solid matter has been deposited. I found this confirmed, and after I had insulated the iron bottle on paraffin supports, I applied a delicate gold-leaf electroscope, and ascertained, when gas was strongly issuing,

\* *Chemische Berichte*, 1890, xxiv. p. 1032.

that in general it was negatively electrified. The gas jet, escaping through the bag, charged the electroscope with positive electricity when very near to the cloth, but frequently, when at some distance, the instrument indicated a negative charge, when struck by the gas-current. When the bag was inserted in a cylinder of narrow copper gauze I got sparks of more than 2 centim. when approaching a metallic conductor. A year ago Wesendonk \* published an extensive research bearing on the question whether electricity is actually generated by friction of gases against metals, already treated by Faraday †, and he came to the conclusion that the gaseous state does not develop electricity, and if indeed a charge manifests itself in the electroscope, it is due to the fact that the gas contains moisture or particles of dust. Experiments were made with air, oxygen, and carbon dioxide under high pressure, and he stated that the latter gas is very apt to develop electricity, because aqueous vapour so easily condenses from the surrounding air about the expanding current of gas which is at very low temperature.

It seems to me that great importance is to be ascribed to the minute particles of *solid* carbon dioxide that certainly are present in the escaping gas, when the liquid substance comes in contact with the aperture and issue-valve, as this is opened. I found, what I have not seen mentioned anywhere else, that the solid carbon dioxide itself is a substance having a great propensity to become electric, as the following experiments show.

When the snow-like solid matter, after it has been taken from the receiving-bag, is put directly on the plate of the electroscope, a strong charge of negative electricity is at once apparent; on placing this instrument under the receiver of an air-pump, the divergence of the leaves rather diminishes when the air is rarefied, and it increases again on admitting air. A disk, formed by strongly compressing carbon dioxide as indicated before, when rubbed with the hands or pressed against the skin becomes negatively electrified and attracts an electric pendulum in a very marked way, even when the

\* Wiedemann's *Annalen*, 1892, xlvii. p. 529.

† Faraday examined air and vapour of water mixed with different substances, and expressed the opinion that when pure they fail to produce electricity; otherwise they communicate a positive charge to the electroscope when it is near to the exit valve, the gas then striking violently against the knob of the instrument. At some distance below he states that this becomes charged negatively, because it acts only as a receiver to the gas already electrified on escaping, whilst in the former case the knob of the electroscope is itself directly electrified by the collision of the gas particles.

friction has been feeble. Rubbing against a zinc or a copper plate acts in the same way, these metals showing positive electrification, and the solid carbon dioxide gets negatively electrified; this is also the case when rubbed with cloth. The readiness with which this substance acquires an electric charge is the more remarkable, as the surface of the disk or cylinder, from the very low temperature, is soon covered with moisture turning to ice particles, but these disappear on moving the hands over the surface. A more complicated case of electrification ensues when the compact disk is simply laid down on the plate of the electroscope. When freshly prepared immediately after the contact, the leaves diverge to an extent corresponding to a difference of potential of at least 200 volts, and more as compared with that effected by a zinc-water-copper battery. It is  $-E$ , and when the disk of carbon dioxide is now removed without touching the metal, the leaves first collapse, and diverge again directly, and now indicate  $+E$ . Sometimes, when the substance has already been exposed to the atmosphere for a time, no charge is immediately produced on touching the electroscope, but afterwards, when it is taken from the instrument, this still shows a positive charge. It is not at once evident how to account for the production of the two opposite electricities in this case\*, as several causes may have been at work. It appears to me that the chief part is played by the carbon dioxide escaping in the state of gas between the disk and the spot where it is in contact with the plate of the electroscope. At this place it is lifted up and down somewhat rapidly by the gas evolved, and it gets a negative charge, for the same reason as when rubbed with the hand as before stated, and no strong motion is required, because of its high electric properties, as I have remarked. The  $+E$  that is free is carried away with the current of gas, and the negative charge of the disk may induce an opposite one in the metallic plate, on which it is lying, and recombination is prevented, because a fresh layer of gas is present and prevents actual contact; the positive charge of course becomes apparent in the electroscope as soon as its inducing electricity is removed with the disk of carbon dioxide. That the action after a certain time is much lessened may perhaps be due to the fact that the copper plate of the electroscope after prolonged contact has become too cold to provoke a rapid evolution of gas, or perhaps the surface of the carbon dioxide, by atmospheric influence, has lost, to some extent, its electric

\* It is necessary, to avoid errors, to make the disk of carbon dioxide neutral after each experiment: this may easily be done by moving it rapidly to and fro in a gas-flame.



property. And the effect in general may be augmented by the friction of the current of gas against the surrounding air of low temperature and saturated therefore with moisture.

*Production of Sound.*—The experiment just described, demonstrating that a piece of strongly compressed carbon dioxide on mere contact with a copper plate may acquire a sufficient electric charge to attract an electric pendulum, and that this should be originated by little impacts from the metal, seems to obtain fresh evidence from another curious fact I often observed on putting this substance in contact with metals, and which consists in a loud sound produced for some time. On further investigation it was soon ascertained that this is due to the thermal conductivity of the metal, acting by increasing the rapid evaporation of the solid matter in different points where the contact was best, and the gas evolved, more or less prevented from easily escaping between the surfaces, was alternately compressed and expanded, producing a vibratory condition of the current of gas. A convenient way to perform this experiment is to take a disk or cylinder of carbon dioxide, very highly compressed, and to lay down on it a small brass sphere with a diameter of 1 cm. ; if the whole system is placed on the resonance box of a tuning-fork (for instance that of  $Ut_4$  answers very well), a loud sound of very high pitch makes itself at once audible throughout the whole room ; if the metal is pressed against the solid substance, it may even become so loud as to be painful to the ear. It slowly dies out as the metal grows too cold to accelerate the evaporation in an effective way, but the sound is again restored when the metal is heated for a moment. Things may be reversed : that means, a cylinder or, still better, a lens of plano-convex form may be set down on a metal surface, and if this consists of a thin copper disk of 8 cm. diameter fixed in its centre, this emits a loud sound, resembling the ringing of a bell. It is easily perceived that the tone is produced at the place of contact where the metallic sphere touches the extremely cold carbon dioxide ; a little cavity is formed (as the metal is comparatively very hot), and this is somewhat closed up by the sphere sinking slowly down ; the occluded gas gets more tension till it can lift the metal, when for a very brief moment it again sinks down, and so on in rapid succession. Of course the same state of things nearly occurs as with a steam-jet escaping downwards from a conical aperture, closed up more or less by a little sphere. It is well known, when high pressure is used, it is not blown away, but remains in front of the opening in a very rapid oscillating condition, and there is also a dull sound often audible.

When the disk of carbon dioxide is not very compact, no sound is produced, because the gas can escape in different ways through the little spaces left, otherwise the intensity of the sound is dependent on the conductivity for heat of the substance brought in contact.

A silver coin, when touching the disk with the flat side, does not act, because it is uneven and little interstices are left, otherwise silver emits loud sounds, and so it is with copper, iron, aluminium; lead produces a dull note and bismuth none at all, as being a very bad conductor unless it has been heated, and then it sounds only for a moment. The carbon rods used in electric lamps remained silent, and also wood, but quartz and rock-salt gave an audible note when a lens of compressed carbon dioxide was applied on them with some pressure. Very beautiful sounds, of the character of those produced with the Trevelyan instrument, were heard when an iron rod was resting with one end on a horizontal cylinder of the compact solid substance and touching with the other a glass plate.

As the escaping gas is the determining cause in all these cases, it is to be expected that other substances, when capable of rapid evaporation, on touching heated metals will also emit sound, and indeed I obtained this very loud when a brass sphere brought to incandescence was firmly pushed down on a piece of mercury bichloride or camphor, and especially on sal-ammoniac, all substances subliming at a red heat; accordingly dense vapours are evolved, when the metal came in contact, and sounded on perforating them.

*Crystallization of Mercury.*—Though the freezing of this liquid metal with the mixture of solid carbon dioxide and sulphuric ether is easily effected, crystallization is not apparent, as the metal then solidifies too quickly. On trying the production of sound with this liquid, I found a very effective method to obtain it crystallized. A disk of slightly compressed carbon dioxide with a cavity was used, and still better was a little cup, 4 centim. high, such as could be formed in a convenient mould of wood, and this I filled with mercury, just as a crucible. A low and distinct sound was given off, and very regular undulations appeared on the bright metal surface, indicating the pulsations provoked by the escaping gas. Though the mercury does not actually touch the sides of the cup (or the cavity on the disk) as a gas layer keeps it away, yet its heat is dispersed by radiation towards the extremely cold surrounding matter, and gradually the vibrations cease. If at this moment the cup is emptied of its still liquid contents, it is seen to be covered inside with

beautiful and sharply defined needles of solid mercury, resembling fern leaves, of more than one centim. in length; the whole mass is coherent and forms now a metal cup, of course with thin walls, that may easily be removed from its mould of solid carbon dioxide and maintains itself during some minutes.

*Effect of Gas and Vacuum Screens.*—One of the most interesting experiments demonstrated by Prof. Dewar at his admirable lectures on liquid air, seems to me the property of a very high vacuum of preventing the access of heat from the surrounding medium to liquids placed inside. Lecturers on low temperatures will not likely have at command such splendid arrangements as Prof. Dewar could dispose of, but the principle of this fact may be illustrated, in a suitable way, with carbon dioxide. I had three glass tubes of 15 millim. diameter constructed, and of equal capacity, and according to Prof. Dewar's device. The first, A, was inside an oblong glass bulb, remaining open, and consequently filled with air that could be exchanged, when desired, for another gas; the second, B, had likewise this bulb, but rarefied with a mercurial pump, thus forming a vacuum-jacket; the third, C, was surrounded by two such concentric vacuum-jackets. Placing them in the same support, next to one another, I put in each the same amount by weight of a mixture of carbon dioxide with sulphuric ether; it is then soon observed, within the quarter of an hour, that A, provided with the air-jacket, is covered outside with a layer of hoar frost; B shows only a slight deposit of condensed aqueous vapour from the atmosphere; and C remains transparent, having no deposit outside. Thus the influence of convection and radiation with regard to a vacuum are visible even at great distances from the lecturer's table.

With the first vessel, A, I carried out another experiment I found suggested in the report of Prof. Dewar's lecture, and bearing on the property of different gases transmitting heat, which they do not all possess to the same extent. In one experiment I put 3 grammes of compressed carbon dioxide in the inner tube of the vessel A, when air was in the bulb, and collected the gas, given off by evaporation at the ordinary temperature, in a glass jar above water. I noted 170 cub. centim. in five minutes. Supplying again the inner tube with the same amount of carbon dioxide and replacing the air by hydrogen, I could collect again in five minutes 250 cub. centim. This increasing proportion shows the great conductivity and convection that hydrogen possesses. On removing the hydrogen and taking carbon dioxide in gaseous form instead of it,

and working also with 3 grammes of solid matter, I now collected only 150 cub. centim., and carbon dioxide in gaseous condition is considered a bad conductor of heat. But the difference in quantity of gas evolved depends also on the power for convection, which will not be equal in the three cases\*.

The following experiment, which is somewhat the reverse of the former, demonstrates the influence of convection in incandescent electric lamps in a striking way. Four similar lamps (16 candle-power and same voltage) were connected in parallel to a dynamo; the first was filled with gaseous carbon dioxide, the second with common coal-gas, the third with hydrogen, and the fourth was kept in normal condition, that is provided with its vacuum around the carbon filament. All carried a little piece of phosphorus at the top of the glass globe on the outside, and now admitting the current in all at the same time, it is observed that the phosphorus is set on fire at different rates; first it burns on the lamp with carbon dioxide, then on that containing coal-gas, and shortly after on the hydrogen lamp, but on the vacuum lamp it remains for a long time intact. In the latter case it may be inferred that the dark heat-rays are very imperfectly transmitted by the vacuum, whilst convection of course must also be very reduced; hence the glass can only receive a small amount of heat, and as in Prof. Dewar's experiment the vacuum prevents the ready access of heat to the extremely cold liquid, in the incandescent lamp, on the contrary, it is an obstacle to the cooling of the filament of carbon. It can therefore attain a high temperature and convert the electric energy it receives, chiefly into radiant light. As for the other lamps, the difference in heat transferred in the same time outside may find its explanation in the well-known experiments of Grove† and the investigation of Clausius; yet it is a curious fact to see the carbon brightly

\* Prof. Kundt described, as long ago as 1877, an experiment of a similar character, employing three vessels of the same size, enclosing at a distance of 3 mm. little tubes each filled with the same volume of sulphuric ether. The vessels were filled respectively with hydrogen, air, and carbon dioxide acting as jackets. Putting all three together in boiling water, heat is transmitted in a different way, as appears when the ether vapour is lighted, and the flame of hydrogen is seen to be the longest, that of the carbon dioxide the smallest, but convection may also influence.

† Grove published his paper on this subject in the Phil. Trans. in 1847, and he determined the amount of heat given off by a platinum wire in different gases to a surrounding mass of water; the experiments with the lamps are in accordance with his results.

glowing in the lamp wherein the phosphorus does not burn, in the lamp with carbon dioxide the filament becomes only dull red, and in the others it remains obscure, but still the phosphorus burns there after a minute.

Though the thermal conductive power interferes, I believe convection to play an important part here, and I venture to predict that, if the incandescent lamp, whilst glowing, could be intensely cooled, by being immersed in liquid oxygen or liquid air, that Prof. Dewar has so readily at hand, it would at once attain a higher illuminating power\*; as convection would still more be lessened, the remaining particles of air and mercury vapour would have their motion almost entirely exhausted. And hence it may be concluded that such a lamp would absorb less electric energy for emitting the same amount of light, when the degree of rarefaction is made the highest possible.

The Hague, April 1894.

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VII. *On an Approximate Method of finding the Forces acting in Magnetic Circuits.* By RICHARD THRELFALL, M.A., Professor of Physics, University of Sydney; assisted by FLORENCE MARTIN, Student in the University of Sydney†.

**D**URING the last three years I have had occasion to design a good many reciprocating electromagnetic mechanisms, and have frequently felt the want of some simple method of making the necessary approximate calculations of magnetic forces.

I have obtained very little satisfaction from the attempts I have made to calculate tractions, proceeding by the method of finding poles and applying the law of inverse squares.

This ill success led me to investigate the applicability of the methods established by Maxwell in the chapter "On Energy and Stress in the Magnetic Field" ('Electricity and Magnetism,' vol. ii. §§ 641-644), with the following results.

§ 1. Theoretical Considerations.

The problem for solution in its simplest form is as follows:—  
"Given an iron anchor-ring uniformly wound and interrupted at one point by an air-gap of any given dimensions—

\* I tried this effect with a mixture of solid carbon dioxide and ether on an incandescent lamp, but the globe becomes covered with frozen aqueous vapour and the mixture itself is a hindrance to judging the brightness acquired; a transparent cold liquid therefore is far more suitable.

† Communicated by the Author.

to calculate the forces tending to draw the ends of the iron ring together when the strength of current flowing in the magnetizing circuit and the data of winding are given.

§ 2. The position established by Maxwell is as follows:—

(1) The laws of magnetic force are such that magnetic forces may be regarded as the expression of a state of stress in the magnetic medium.

(2) The medium is stable under such a distribution of stresses.

(3) A series of expressions may be found for the stresses at any point in the magnetic field.

§ 3. Maxwell's investigation does not explicitly include the case of a body with inconstant permeability; but I cannot find that this in any way vitiates the argument. Professor J. J. Thomson shows ('Applications of Dynamics to Physics and Chemistry,' § 33) that Maxwell's results may be considered

as being derived from the existence of a term  $\frac{1}{8\pi} HB$  in the

Lagrangian function for unit volume of a magnetic field. If the permeability is a function of the induction, however, in

any part of the field, the more general expression  $\frac{1}{8\pi} \int H dB$

must be substituted for the above and the results modified accordingly. I have not succeeded in doing this. It appears, therefore, that Maxwell's system as applied to iron does not cover all the ground, because a modification must be introduced on account of the inconstancy of the permeability, and also on account of the Villari effect as shown by Professor Thomson. There may also be other undiscovered additions to make.

§ 4. A great step is necessary to pass from Maxwell's position—that magnetic forces may be regarded as the expression of stresses in the field—to the position that magnetic forces are such an expression. There is all the difference that exists between a theory and a fact.

Everything, however, tends to show that the fact is that the theory is probably true so far as it goes, and we will therefore provisionally adopt it, and see first what additional hypotheses are necessary. It is obvious at once that the stresses are "stresses in a medium," while the forces are mechanical forces acting on matter. We must therefore consider that the medium is "attached" to matter so as to allow the stresses to appear as forces. Now the stresses in the medium depend on the nature of the matter which is permeated by the medium. Thus in the cut anchor-ring

referred to above (§ 1), the stresses in the medium in the air-gap are not at all the same as the stresses in the medium in the iron. In our entire ignorance of the connexion existing between the medium and matter, it is not to me at all clear that, in calculating the magnetic forces tending to close the ring, we ought to consider the stresses in æther in air, and those alone. It is at all events conceivable that the nature of the connexion between the medium and the iron may be modified in some manner by the internal stresses in the iron. Also the ordinary laws of magnetic and electromagnetic action received their experimental demonstration at low inductions; and we have no right to say, without experimental evidence, that some terms not contemplated by Maxwell might not begin to produce effects on the stresses in air at high inductions. In the parallel case in iron such stresses do in fact occur.

I therefore attribute great importance to the experimental verification of the results deduced from Maxwell's theory as applied to the traction between iron bars in general, and especially at high inductions.

§ 5. *Experimental position.*—The simplest case is that of the traction between two plane faces of iron, the faces being either the terminals of otherwise closed iron circuits, or of very long bars.

The case of the ring has been implicitly investigated by Bidwell (Phil. Trans. 1886); and the case of short bars by Bosanquet explicitly (Phil. Mag. 1886, vol. xxii.). The latter is the only investigation I know of in which simultaneous observations of Induction and Tractive force were made. In both cases Maxwell's theory leads to the expression

$$F = \frac{B^2 A}{8\pi}$$

for the force in air between two opposing plane faces of iron, infinitesimally separated,  $A$  being the area of the faces and  $B$  the (uniform) induction-density.

The net result of Bosanquet's work was to show:—

- (1) When  $B$  is below 5000 the Traction observed are generally much too large.
- (2) The formula does not hold when the air-gap is appreciable.
- (3) It holds within about 5 per cent. up to very high inductions.

It is obvious, therefore, that there is room for more work on the subject.

§ 6. For the reasons given I felt very strongly that it was

necessary to establish the truth, or rather the approximate exactness, of the theory in the simple case studied by Bosanquet before going on to apply it to other and more complicated cases.

Consequently I investigated the following matters :—

- (1) Influence of length of bars.
- (2) Influence of kind and size of pole-pieces.
- (3) Influence of imperfections in the ballistic method.
- (4) Cause of Bosanquet's failure to obtain agreement with theory at low inductions.

- (5) Cause of similar failure (?) with an appreciable air-gap.

§ 7. *Method of Experimenting.*—I wound a number of solenoids on brass tubes, placed the iron bars to be investigated axially in these solenoids, observing the usual precautions, and measured the force (by calibrated spring-balances) requisite to pull the bars apart, the force being applied scrupulously parallel to the axis of the bars by means of links, pulleys, and strings. Great attention was paid to the state of the cut surfaces. I tried surfaces of all kinds.

- (a) Merely filed by watchmaker's finishing files.
- (b) Ground on flat whetstones to a surface-plate.
- (c) Scraped to a surface-plate.
- (d) Ground by emery wheels.
- (e) Turned flat—to a surface-plate. This takes a little skill.

(f) Optically ground by emery and diamond-dust and finished with putty-powder.

This requires a note. Of course the bars must be provided with shoes of many times their diameter to make the process a success, and these shoes must be of similar material to the bars. In order to save circumlocution I may state that both I and my assistant Mr. Cook are fairly expert at this kind of work, and we met with no real difficulty. The use of diamond-dust instead of emery saves a little time, but makes it more difficult to get a good result. I obtained two sets of bars with properly ground faces. One of these sets was of hard iron, and was not so good as Brashear's celebrated test-plates, on account of a slight convexity on the part of one surface and a corresponding concavity on the part of the other. The other pair of bars were of soft Swedish iron well annealed; they were less than 1 centim. in diameter, and about 60 centim. long. The surfaces were as good as the test plates, *i. e.* perfect according to the present state of the art. I have little doubt that they are as good soft iron surfaces as have ever been prepared. This means that there was no inequality comparable with a wave-length of sodium-light on either surface.



The bars were kept straight and aligned by well-fitting glass, or brass, or fibre tubes at the plane of contact. The fit was always just so good that no correction for friction was necessary. The magnetizing current was measured by a Siemens dynamometer, which was compared with suitable members of a chain of Kelvin balances. It was found that in this instrument the readings were correct within the limits of accuracy of reading. The current was supplied by storage-cells.

The induction-coils were wound on brass bobbins with proper precautions. The bobbins were of different diameters, and were compared ballistically, and found to give identical results; hence it was concluded that they were all free from leakage errors.

The ballistic galvanometer was a fine instrument, specially made for this kind of work. It was calibrated by turning over a large coil which was splendidly wound, and which has been checked in many ways. I made use of the values for the vertical force obtained about nine months ago by Mr. Farr, from a long series of experiments in my laboratory under the best and most careful conditions, and with the Kew apparatus. In all cases the induction-throw on the galvanometer was checked by reversal of the galvanometer-corrections, except when experiment showed that nothing was gained by such reversals, the instrument being in another part of the laboratory to the magnetic system. In all cases large resistances from a box of coils, constructed and calibrated by myself from Cambridge standards, were inserted in the circuit so as to give the best range for the galvanometer.

§ 8. *Results of Experimenting.*—The general result was that I got rather worse agreement than was noted by Bosanquet, especially at low inductions. I therefore set myself to find out the reason of this. I am ashamed to say how long it took me to clear up the difficulty. I investigated the following possible causes.

(1) Imperfection of galvanometer law. This was got over by adjusting resistances till the same deflexion was obtained both on turning over the earth-inductor and on magnetizing the iron.

(2) Effects due to residual state of the iron. These were got rid of by demagnetizing the iron by an alternator and slide-resistance, and observing magnetizations with the current in both directions, and also on reversal. By comparing the three sets of deflexions I assured myself that the discrepancy was not due to any error of this kind. A similar procedure when taking the tractions led to a like result.

(3) By using induction-coils of different diameters I assured myself that I was really measuring the operative inductions.

(4) The state of the surface of the bars is an important matter. If the ends are rough, of course the contact is at points. This leads to a concentration of induction at these places, and is a very constant source of error. My best bars, however, gave just as anomalous results as my roughest ones, so that the deviation could not be attributed to this cause.

(5) Finally I tried, without much confidence, the effect of a small indirectness of pull. This was done by winding two wide solenoids and leaving sufficient space between their ends to see what was going on at the point of junction; a gas-flame was put on the side of the junction, remote from the observer.

It was then found that one side of the bar which was being pulled off invariably remained in contact after the other side had slightly separated—when this was prevented by slightly guiding the spring-balance by hand, the agreement was as good as at higher inductions. The explanation is now obvious. If the bars separate slightly just at one side, two things happen. (1) The total reluctance of the circuit increases. (2) The induction concentrates at the parts in contact. At low inductions the effect of (2) overpowers that of (1). At high inductions, when the permeability of the iron becomes less, the induction is less free to distribute itself, and also the traction of the bars being greater, the phenomenon does not begin to manifest itself till rupture is just about to be produced, or it produces a very much smaller percentage error. Of course all this might have been foreseen, but one's experience with strong magnets—in which case it is notorious that it is much more difficult to pull off an armature straight than sideways—misled me.

On examining other bars which had given similar results at low inductions, I found I could similarly diminish or increase the apparent traction by varying very slightly the direction of pull. Thus with a pair of flat-ended bars and an induction of about 3000 C.G.S. the calculated pull was one pound seven ounces; but the observed pull was always over two pounds, and in some experiments about three pounds. On guiding the bars so that no wedge-shaped gap appeared, the traction could be got down to about one pound eight ounces. I do not think it is possible to get much closer than this, for if proper arrangements are made to absolutely ensure a really true and rigid separation, friction would inevitably come in

to introduce errors. My results at higher inductions were so similar to Bosanquet's that they are not worth reproducing.

§ 9. With regard to the formula not applying with non-magnetic gaps of sensible dimensions parallel to the lines of induction—as when Bosanquet separated the bars by wood and paper—the explanation is obvious. The lines of induction no longer leave the surfaces normally, and the conditions postulated by the formula are not in existence.

§ 10. Resulting position of the Theory.

When the bars are in contact, the stress theory, and what I will call the magnetic fluid theory, lead to the same result. Which is true certainly within about five per cent., and may be exactly true.

In any case, measuring tractions is not the way to get accuracy, though I have no doubt that rather better results could be got by going into the matter more elaborately than was done either by Bosanquet or myself.

In what follows I shall suppose that the theory is true, and that the real cause of magnetic forces is to be sought in some condition of the æther mechanism which receives a sufficient statistical definition from the Induction Diagram.

§ 11. The effect of varying the kind of iron employed should be the same as varying the induction-density—at least in so far as the phenomenon can be considered to depend on permeability. I used induction-densities of from 2000 to 18,000, but could not detect any effect—when the cause of error referred to above was eliminated. I also used all kinds of iron, from annealed Swedish iron to ordinary cast iron. I varied the lengths of the bars from 60 cm. to 6 cm.—and the diameter from about 2 cm. to about .6 cm.

In no case could I detect any deviation from the predicted traction which could not be explained by unavoidable experimental errors. With short bars and high inductions necessitating the use of very strong fields, some induction is included by the testing-coil which does not help the traction and which tends to make the calculated traction appear too large. When this source of error was eliminated, no greater discrepancies were observed with short bars than with long ones.

§ 12. I conclude therefore

(1) The traction produced by a given tube of induction when running out of air into iron and crossing the surface normally is independent of the nature of the iron, or of its form. I had a difficulty in bringing myself to believe this, but the conclusion seems inevitable.

*Corollary* (1). The magnetic forces are independent of the stresses in æther inside the iron.

*Corollary* (2). Setting aside Professor J. J. Thomson's stresses, the æther stress in air is less than that in iron—assuming that Maxwell's "magnetic material" sufficiently represents iron. The difference of tensions is

$$\frac{B^2}{8\pi} - \frac{1}{4\pi} (BH - \frac{1}{2}H^2),$$

or

$$\frac{(B-H)^2}{8\pi}.$$

This is an unbalanced stress ; and if the lines of induction in the iron give rise to forces similar to those produced in air, this must mean that the boundary tends to be pulled off the iron. Taking Professor Thomson's stresses into account, this effect may easily be reversed in any actual case.

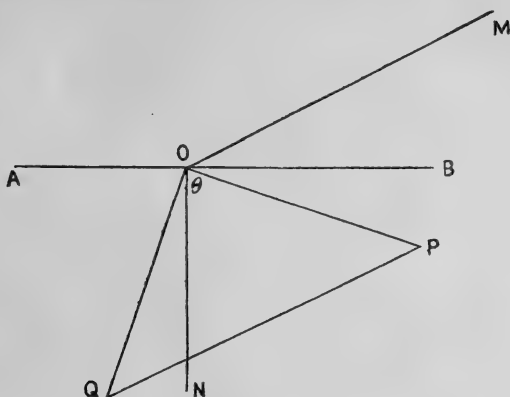
Referring to Professor Thomson's investigation (Physics and Chemistry), I cannot avoid the impression that there still remains a set of stresses depending on the variation of elastic constants with temperature. This would further complicate matters.

§ 13. Each tube of induction is therefore a tube of force within the usual definition ; but it does not follow that the only forces are those represented by the tubes of induction. If the tubes leave the iron surface normally, then the pressural forces are tangential and we get the formula we have been using ; and similarly if the tubes of induction are tangential (*i. e.* when the infinitesimal air-gap separates similar poles), the pressures operate alone, and we have a repulsion equal to the former attraction as in the elementary theory. If the tubes of induction leave the iron at any angle to the surface between 0 and  $\pi/2$ , we must consider the effect of the pressural forces.

To calculate these effects it is convenient and perhaps correct to assume that just as the internal stresses of the iron do not affect the forces which are the expression of the external æther tensions, so they do not affect the forces corresponding to the hydrostatic pressures. If, therefore, we consider a line of force running out of iron into air and making an angle  $\theta$  with the normal, we can estimate the direction and magnitude of the magnetic forces at once, thus :—

Let AB be the trace of a plane boundary between air and iron, and ON a normal drawn outwards into air. Let OP be a vector in the plane of the paper representing the tensional

force per unit area at a point about O. Draw OQ perpendicular to OP and in the plane of the paper. Then the pressural forces lie in a semicircle of which OQ is a radius, and whose plane contains OQ. Since the pressures are symmetrical with respect to OQ, OQ is their resultant, and



by the theory this is equal to OP—so that OQ is the vector representing the pressures. A force represented by OM equal and parallel to PQ is therefore the resultant force, and clearly in this case is a repulsion whose magnitude along the normal produced is

$$OP \cdot \sqrt{2} \cos \left( \frac{3\pi}{4} - \theta \right),$$

an expression which gives no normal component at all when  $\theta = \pi/4$ . The force is therefore an attraction or repulsion according as  $\theta$  is less or greater than  $\pi/4$ —and a shear at this point. I tried to observe this, but could not get the lines to leave the surface at the exact angle. However, the above way of looking at the matter is convenient when filings are used to trace the direction of the induction. This expression has been pointed out to me by Mr. Pollock as identical with that given by Maxwell's general formula in § 643 for the special case here considered.

It is now evident why it was that Bosanquet got results differing from those calculated from the formula for normal inductions, because, as filings show, a very small gap is sufficient to produce a marked spreading of the field.

§ 14. By observing the distribution of filings about different air-gaps, it appeared probable to me that the following proposition might be true—as referring to bars of different

diameters:—"With similar pole-faces and the same permeability and induction-density, the induction (or filing) diagrams are similar when the length of the air-gap is the same fraction of a standard dimension of the pole-faces."

If this be true, it follows as a consequence that with similar air-gaps at similar induction-densities, the traction is the same fraction of the traction with the poles in contact, whatever be the actual dimensions of the poles.

The greater part of the experimental work I have to offer refers to this point, for, if established, we clearly have a method which will enormously facilitate the calculation of magnetic forces.

§ 15. The observations made on this subject are sufficiently detailed in the Tables I. to XIII., and the results will be understood by looking at the curve.

The tractions were measured by spring balances as before, measured pieces of brass being inserted between the pole-faces. In a series of observations the induction was kept constant by varying the magnetomotive force.

The observations were taken just as in the previous case. A little care is necessary in defining what is meant by the total induction. If the bars are long and thin, then of course the solenoidal condition is fulfilled pretty closely, and there is no ambiguity; but with large air or brass gaps—say, amounting to two diameters of the bars—the lines begin to leave the iron just in front of the middle point of each bar (at all events when the bars are about 50 diameters long). The "total induction" therefore has no very exact meaning with respect to the iron, unless it be specified where it is to be measured.

At the time the experiments were made, I did not (as I now consider) sufficiently attend to this point, though I used a testing-coil of about four times the diameters of the bars, and kept the coil just to one side of the gap when the latter was large. It is probable, therefore, that I have considerably overestimated the tractions with the larger air-gaps, for the induction must have been greater than I took it to be. I have decided not to re-investigate this point, for the curve is of use in giving approximate ideas of tractions only; and no one, after looking at it, would design a mechanism with air-gaps as long as those which are probably inaccurate. I have made a little allowance for this (most unscientifically of course) in drawing the curve. In fact my suspicions were first aroused by examining the part of the curve corresponding to the larger air-gaps.

It will be seen that I examined a good many cases, and the

results show that when the non-magnetic field is of sensible dimensions, the differences in the permeability of the samples examined do not lead to any very abnormal results. The curve is drawn by reduction for a bar one centimetre in diameter; and the air-gaps, which must be expressed in diameters, appear therefore in centimetres. The ordinates give the values of the tractions at corresponding points in terms of the calculated tractions when the surfaces are in contact.

One set of observations refers to square bars. In order to utilize the results, I assumed that the field would be distributed very much as if the bar were round and of a diameter equal to the mean of the diameters of the inscribed and circumscribed circles.

To use the curve it is only necessary to express the length of the air-gap as a fraction of the diameter of the pole-face, and refer to the table to find the proper factor to multiply the traction with the bars in contact at the proposed induction.

It will be seen that the factor is practically the same for all inductions—hence one curve only is given.

§ 16. In general it is more convenient to take the magneto-motive force as given; and in this case the induction cannot be estimated without a knowledge of the reluctance of the circuit. Now methods of building up the characteristic curve of the magnet have been given when the air-gaps are narrow by Drs. J. and E. Hopkinson and others; but I thought that I might possibly be able to extend the method of similar systems so as to include air-gap reluctances. In similar induction systems at constant induction-density, the reluctances of the gaps should be, roughly, inversely as the linear dimensions. I examined three sets of bars to see how near such an approximation really was, but it will be noticed that the results would not reduce so as to give a single curve by any such simple process. The curves are therefore kept separate; they cover bars of from about one to three centim. in diameter. The induction was in these cases correctly measured at the centres of the bars. It was necessary to use the ampere-balances to get a sufficiently accurate knowledge of the magnetizing currents. The results are contained in Tables XIV. to XVI., and are also plotted for the mean of all inductions. The reluctance of the iron and air circuits was measured before the bars were cut and plotted against inductions. It was assumed that by using bars of the length employed, the air reluctance (other than that at the gap) would not be materially changed by pushing the bars up to

2 diameters apart. The proper reluctance for the iron and air circuits was taken from the curve in finding the reluctance of the air-gap.

Except with the largest bar, there is no definite indication of the reluctance depending on the induction-density. In this case separate curves might have been drawn, but I did not think it worth while to introduce a fresh sheet of curves.

I am not sure that a real reduction in air-gap reluctance at about  $\cdot 2$  diameter has not been smoothed out; but as the observations are marked on the curves, any one will be able to form his own opinion.

It will be noticed that the curvature becomes very great when the air-gap amounts to about  $1\cdot 5$  diameter. It is, perhaps, not too much to say that the reluctance increases very fast as the gap increases to  $\cdot 2$  diameter, after which it increases more slowly up to about 1 diameter, and then remains roughly constant.

§ 17. I do not know whether a unit of reluctance has yet been adopted. It has been necessary for me to use one, however, and I take as unit reluctance that reluctance through which unit magnetomotive force produces unit induction. By unit magnetomotive force I mean that magnetomotive force whose C.G.S. value is unity—*i. e.*, that produced by  $\frac{1}{4\pi}$  C.G.S. turns. If the permeability of air be taken as unity, then one cubic centimetre of air has unit reluctance on this system. There are, of course, other ways of defining unit reluctance; but this is, I think, the only one that gets rid of the  $4\pi$  and leads to an easily realizable material standard.

§ 18. The reluctance curves and traction curves are not unlike each other in general form, and enable us to draw some practically valuable conclusions as to the design of magnets intended to operate over air-gaps. For instance, with a given total induction the force at contact is inversely as the area, but the traction curve shows that this principle must not be pushed too far when we consider traction over an air-gap. Thus, I am told (though I do not believe it) that rock-drills will not work with a shorter stroke than five inches; the traction curve shows at once that for a given induction (a case which does not practically occur in every instance) it is possible to make the pole-pieces too small, if we wish to get the maximum work done during the stroke. This is independent of considerations arising when magnetomotive force, and not induction, is given.



TABLES I. to XIII.—TRACTION OVER AIR-GAP.

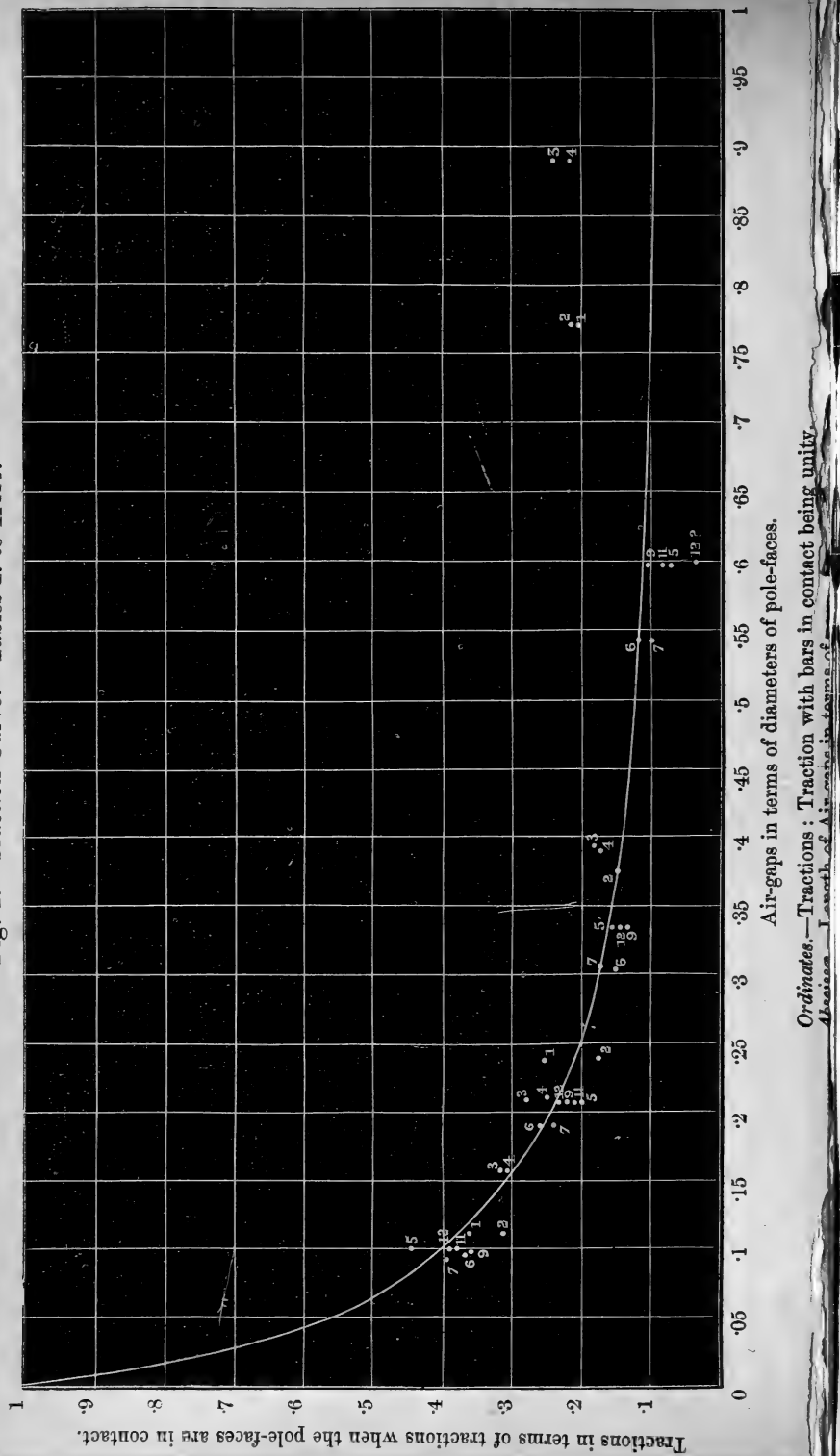
Length of Bars.	Diameter of Bars.	Area of Pole-face.	State of Pole-face.	Thickness of Distance- pieces in centimetres.	Gap as fraction of Diameter.	Factor for multiplying Traction with no Air-gap.	Computed Traction, in lbs.	Observed Traction.	Remarks.
30 cm. each.	.895 cm.	.629 cm.	Ground on stone.	0	0	1	12.28	4.5 lbs.	TABLE I.
"	"	"	"	.1	.11173	.3665		3.11 "	B=14770.
"	"	"	"	.214	.2391	.25325		29.8 oz.	
"	"	"	"	.338	.3777	.1517		21.17 "	TABLE II.
"	"	"	"	.69	.7710	.10775			B=4646.
"	"	"	"	0	0	1	3.068	15.75 oz.	
"	"	"	"	.1	.11173	.3208		9.0 "	
"	"	"	"	.214	.2391	.1833		7.125 "	
"	"	"	"	.338	.3777	.1451		5.687 "	
"	"	"	"	.69	.7710	.11585		7.167 "	Erroneous, due to lines missing the [coil.
"	"	"	"	1.466	1.638	.1460			
28.13 cm. each.	1.2507 cm.	1.227 cm.	Optically ground, not quite flat.	0	0	1	8.99	2.915 lbs.	TABLE III.
"	"	"	"	.192	.1593	.3241		39.42 oz.	B=9052.
"	"	"	"	.256	.2124	.2740		26.9 "	
"	"	"	"	.466	.3808	.1870		20.115 "	TABLE IV.
"	"	"	"	1.074	.8912	.1397			B=12790.
"	"	"	"	0	0	1	17.94	5.679 lbs.	
"	"	"	"	.192	.1593	.31655		4.381 "	
"	"	"	"	.256	.2124	.24415		3.119 "	
"	"	"	"	.466	.3808	.1739		34.32 oz.	
"	"	"	"	1.074	.8912	.1196			

# TRACTION OVER AIR-GAP (continued).

Length of Bars.	Diameter of Face of Bars.	Area of Pole-face in square centim.	State of Pole-face.	Thickness of Distance-pieces in centim.	Gap as fraction of Diameter of Pole-face.	Factor for multiplying Traction with no Air-gap.	Traction observed.	Traction computed.	Induction Density.	Remarks.
26.77 cm. each.	1.02 cm.	.81713	Perfect. Round [ends.	0	0	1	10.0 lbs.	9.47 lbs.	11358	TABLE V. Inductions probably all rather too large. Coil of large dimensions used.
"	"	"	"	.1	.098	.446	4.34 "	"	"	
"	"	"	"	.212	.208	.2004	1.95 "	"	"	
"	"	"	"	.340	.333	.1584	24.0 oz.	"	"	
"	"	"	"	.610	.598	.077	11.72 "	"	"	
"	"	.8584	Finely milled.	0	0	1	14.5 lbs.	13.01 lbs.	13019	TABLE VI. The "diameter" of the square is taken as the mean of the diameters of the inscribed and circumscribed circles. Induction probably overestimated.
"	Square bars with square ends. Length of side of square .9265 cm. Diam. of mean circle 1.1184 cm.	"	"	.1	.089	.3689	4.8 "	"	"	
"	"	"	"	.212	.1895	.2537	8.3 "	"	"	
"	"	"	"	.340	.304	.15375	2.0 "	"	"	
"	"	"	"	.610	.545	.1167	25.0 oz.	"	"	
One Bar = 26.77 cm. The other = 13.3 cm.	"	"	"	0	0	1	14.7 lbs.	13.01 lbs.	13019	TABLE VII. Induction effects considerably overestimated, owing to the necessity of using a very strong field with the wider gaps.
"	"	"	"	.1	.089	.3984	5.118 "	"	"	
"	"	"	"	.212	.1895	.2422	3.151 "	"	"	
"	"	"	"	.340	.304	.1568	2.04 "	"	"	
"	"	"	"	.610	.545	.097	1.26 "	"	"	
"	Round faces; diam. 1.02 cm.	.81713	Perfect.	0	0	1	11.975 "	13.825 lbs.	13756	TABLE VIII. Induction overestimated, owing to testing-coil being too large for the strong field employed.
"	"	"	"	.1	.098	.2966	4.1 "	"	"	
"	"	"	"	.212	.208	.1808	2.5 "	"	"	
"	"	"	"	.340	.333	.1329	1 lb. 11 oz.	"	"	
"	"	"	"	.610	.598	.07217	1 lb.	"	"	
"	"	"	"	0	0	1	.....	4.208 lbs.	7590	Not used for curve.
"	"	"	"	.1	.098	.3639	1 lb. 8.5 oz.	"	"	
"	"	"	"	.212	.208	.2228	15.0 oz.	"	"	
"	"	"	"	.340	.333	.1522	10.25 "	"	"	
"	"	"	"	.610	.598	.1040	7.0 "	"	"	TABLE IX. The Induction being lower, the results are more reliable, except with the longest gap.

Length of Bars.	Diameter of Face of Bars.	Area of Pole-face in square centim.	State of Pole-face.	Thickness of Distance-pieces in centim.	Gap as fraction of Diameter of Pole-face.	Factor for multiplying Traction with no Air-gap.	Traction observed.	Traction computed.	Induction Density.	Remarks.
One Bar = 26.77 cm. The other = 13.3 cm. "	Round faces; diam. 1.02 cm. " " " " "	.81713 " " " " "	Perfect. " " " " "	0 .1 .212 .340 .610 0 .1 .212 .340 .610 0 .1 .212 .340 .610 0 .1 .212 .340 .610 0 .1 .212 .340 .610 0 .1 .212 .340 .610	0 .098 .208 .333 .598 0 .098 .208 .333 .598 0 .098 .208 .333 .598 0 .098 .208 .333 .598 0 .098 .208 .333 .598 0 .098 .208 .333 .598	0 .2752 .1682 .1093 .0643 1 .2524 .1464 .1033 .058 1 .385 .208 .145 .086 1 .390 .231 .1528 .04027	12.44 lbs. 3.87 " 2.34 " 1.52 " 14.302 oz. 15.88 lbs. 5 " 2.9 " 32.75 oz. 18.38 " ..... 8.688 oz. 4.7 " 3.28 " 1.95 " 18.17 lbs. 6.7 " 4 " 48.42 oz. 12.76 "	13.91 lbs. " " " " 19.81 lbs. " " " " 22.535 oz. " " " " 17.25 lbs. " " " "	13799 " " " " 16465 " " " " 4391 " " " " 15370 " " " "	<p>TABLE X. Exactly the same objection as in the case of Table VIII. Not used for curve.</p> <p>TABLE XI. Suffers from the same defects as Tables VIII. and X. B is probably too large by say 10 % owing to the coil used being of too large a diameter for the very strong field of 500 C.G.S. These results are normal, though taken with wide coil. Not used for curve.</p> <p>TABLE XII. Included in curve because the field was low enough not to cause serious or even appreciable errors.</p> <p>TABLE XIII. A testing-coil, having internal diameter 1.7 cm. and outer diameter 2.3 cm., with 400 turns, was used. The field reached 500, and everything was very hot. This prevents much weight being attached to the traction at greatest distance. Numbers used on curve.</p>

Fig. 1.—Traction Curve. Tables I. to XIII.



Ordinates.—Traction: Traction with bars in contact being unity.  
Abscissae.—Length of Air-gaps in terms of pole-faces.

TABLE XIV.

Length of Air-gap in centimetres.	Length of Air-gap in terms of diameter of pole-face.	Current in magnetic solenoid in amperes.	Deflexion of Ballistic Galvano-meter in scale-divisions.	Total Induction corresponding to observed throw of ballistic needle.	Reluctance of whole circuit in C.G.S. units. [Electro-magnetic.]	Reluctance of Air-gap in C.G.S. units.	Deducted Reluctance for bars one centimetre in diameter.	Induction Density.	Remarks.
0	0	.18	23	2887	.0881	0	0	2709	Bar 63 cm. long. Diam. of face [1.165 cm.
"	"	.24	32	4017	.0844	"	"	3769	Bar uncut.
"	"	.48	82.5	8255	.0822	"	"	7743	
"	"	.72	98.5	11739	.0867	"	"	11037	
"	"	1.0	111.25	13967	.1012	"	"	13103	
"	"	1.25	134.5	16887	.1046	"	"	15841	
.082	.0704	.34	55.25	6718	.1430	.0608	.07083	6303	
"	"	.6	94.5	11492	.1476	.0609	.07095	10780	
.218	.1871	1.0	134.5	16356	.1728	.0682	.0794	15343	
"	"	.4	59	7175	.1576	.0754	.0878	6730	
"	"	.66	94	11431	.1632	.0765	.0891	10723	
"	"	1.0	130	15809	.1788	.0742	.0864	14830	
.426	.3656	.4	55.5	6749	.1675	.0853	.0994	6331	
"	"	.7	93.75	11400	.1735	.0868	.1011	10695	
"	"	1.0	123.5	15019	.1880	.0834	.0972	14089	
.61	.5237	.42	56.25	6840	.1735	.0913	.1064	6417	
"	"	.72	95.5	11613	.1752	.0885	.1031	10895	
"	"	1.0	121	14579	.1939	.0893	.1040	13677	
.94	.8069	.44	57.5	6992	.1779	.0957	.1115	6559	
"	"	.72	92.5	11249	.1809	.0942	.1097	10553	
"	"	1.0	119	14471	.1953	.0973	.1133	13576	
2.0	1.716	.44	54.25	6597	.1885	.1063	.1238	6188	
"	"	.74	89.25	10853	.1927	.1060	.1235	10181	
"	"	1.0	114.5	13924	.2030	.1050	.1223	13062	

TABLE XV.

Length of Air-gap in centimetres.	Length of Air-gap in terms of diameter of pole-face.	Current in magnetic solenoid in amperes.	Deflexion of Ballistic Galvano-meter in scale-divisions.	Total Induction corresponding to observed throw of ballistic needle.	Reluctance of whole circuit in C.G.S. units. [Electro-magnetic.]	Reluctance of Air-gap in C.G.S. units.	Deducted Reluctance for bars one centimetre in diameter.	Induction Density.	Remarks.
0	0	.16	27.25	1986	.1138	.....	.....	2982	Bar uncut. 63 cm. long. .921 cm. [diam.
"	"	.24	45.25	3298	.1029	.....	.....	4951	Half solenoid.
"	"	.4	69.5	5066	.1116	.....	.....	7604	" "
"	"	.6	99.5	7253	.1169	.....	.....	10886	" "
"	"	.5	129.25	9422	.1500	.....	.....	14143	Whole solenoid.
"	"	1.0	154.5	11263	.2570	.....	.....	16905	
.082	.0890	.2	45	3213	.1760	.0731	.06732	4822	
"	"	.32	73	5154	.1755	.0639	.0588	7737	
"	"	.5	105	7414	.1907	.0738	.0679	11130	
"	"	.66	129	9109	.2048	.0548	.0505	13670	
.218	.2367	.2	40.75	2877	.1965	.0836	.0862	4319	
"	"	.34	71	5013	.1918	.0801	.0738	7525	
"	"	.54	105	7414	.2059	.0890	.0819	11130	
"	"	.72	128.75	9087	.2240	.0740	.0682	13640	
.426	.4625	.2	40.5	2860	.1977	.0948	.0873	4293	
"	"	.36	71.75	5066	.2009	.0893	.0822	7600	
"	"	.54	100.5	7096	.2152	.0982	.0904	10652	
"	"	.72	125.75	8879	.2293	.0793	.0730	13329	
.61	.6623	.24	45.5	3213	.2112	.1083	.0997	4822	
"	"	.36	70.75	4995	.2037	.0921	.0848	7498	
"	"	.54	100.5	7096	.2151	.0982	.0904	10652	
"	"	.7	121.75	8596	.2302	.0802	.0738	12904	
.94	1.0206	.2	39.5	2789	.2027	.0998	.0919	4186	
"	"	.36	70	4943	.2059	.0943	.0869	7419	
"	"	.54	99.75	7043	.2168	.0999	.0920	10572	
"	"	.72	124.25	8774	.2320	.0820	.0755	13169	
2.0	2.171	.22	38.5	2718	.2288	.1259	.1160	4081	
"	"	.38	67.25	4748	.2262	.1146	.1055	7127	
"	"	.6	102.25	7220	.2355	.1186	.1092	10840	
"	"	.9	135	9532	.2670	.1170	.1077	14310	

TABLE XVI.

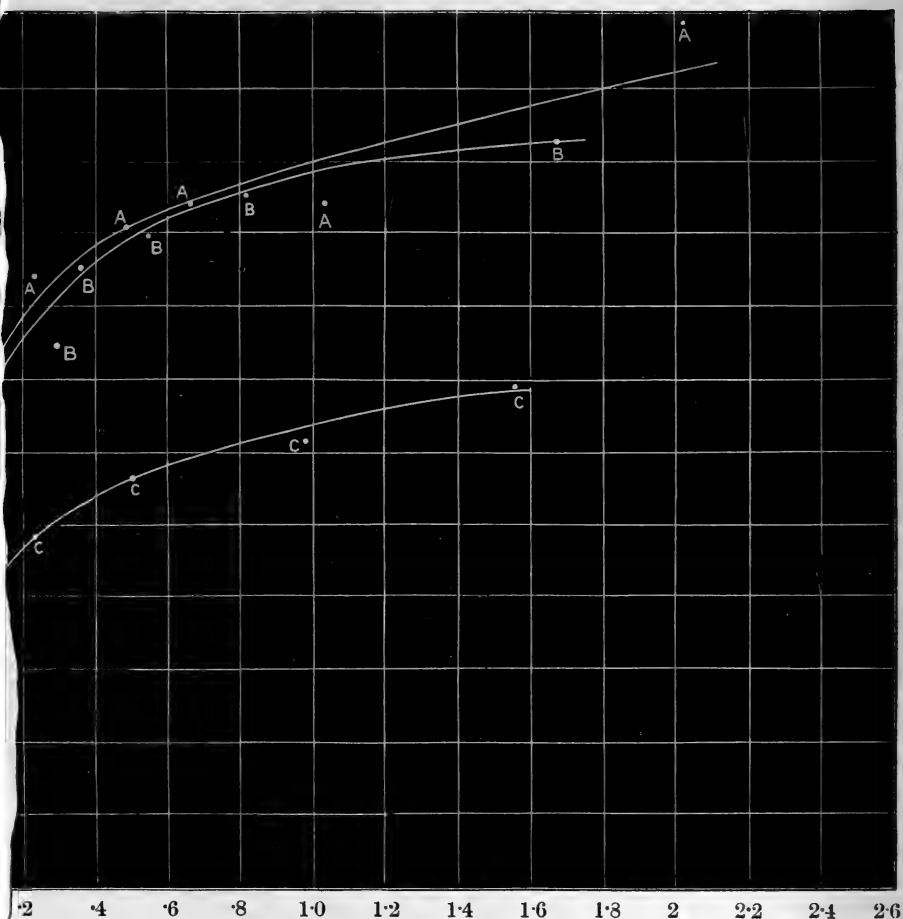
Length of Air-gap in centimetres.	Length of Air-gap in terms of the diameter of the bars.	Current in magnetic solenoid in amperes.	Deflexion of Ballistic Galvano-meter in scale-divisions.	Total Induction corresponding to observed throw of ballistic needle.	Reluctance of whole circuit in C.G.S. units. [Electro-magnetic.]	Reluctance of Air-gap in C.G.S. units.	Deducted Reluctance for bars one centimetre in diameter.	Induction Density.	Remarks.
0	0	·30	28·75	29740	·02852	.....	.....	4632	Bar of "Best" iron annealed.
"	"	·64	51	63863	·02830	.....	.....	9945	Length 91·5 centim.
"	"	1·8	88	110200	·0462	.....	.....	17161	Diameter 2·8595 centim.
"	"	2·5	93·25	116770	·0605	.....	.....	18185	Length = 32·75 diameters.
·308	·1077	·6	21·25	26610	·06374	·0352	·10065	4143	Solenoid 60 centim. long.
"	"	1·5	55	68872	·06157	·0310	·0887	10725	placed symmetrically.
·686	·2399	3·6	85·5	107070	·09505	·0500	·143	16673	
"	"	·8	25·5	31932	·07082	·0423	·121	4972	
"	"	1·7	54	67619	·07107	·0420	·120	10530	
"	"	4·0	86·75	108630	·104	·0591	·169	16917	
1·408	·4924	·9	24·75	30993	·08209	·0536	·153	4826	
"	"	1·8	51	63863	·07968	·0511	·146	9945	
"	"	4·2	87	108950	·1089	·0634	·181	16965	
2·850	·9966	·9	23·25	29114	·08739	·0588	·168	4533	
"	"	2·0	52	65115	·08683	·0585	·167	10140	
"	"	4·3	86·25	108010	·1125	·0665	·190	16820	
4·5	1·5737	1·0	24·25	30363	·09311	·0646	·185	4728	
"	"	2·2	51·75	64795	·09598	·0676	·193	10090	
"	"	4·6	86·75	108630	·1197	·0737	·211	16917	

TABLE XVII.—Air-gap Reluctance. General Table.

A. Bar .921 cm. diameter ; 63 cm. long.					B. Bar 1.165 cm. diam. ; 63 cm. long.			
Air-gap in terms of the diameter of the pole-face.	Air-gap Reluctance. Induction-density about 5000.	Air-gap Reluctance. Induction-density about 7500.	Air-gap Reluctance. Induction-density about 11000.	Air-gap Reluctance. Induction-density about 13600.	Air-gap in terms of the diameter of the pole-face.	Air-gap Reluctance. Induction-density about 6000.	Air-gap Reluctance. Induction-density about 10500.	Air-gap Reluctance. Induction-density about 13000.
.08903	.0731	.0639	.0738	.0548	.0704	.0608	.0609	.0682
.2367	.0936	.0801	.0890	.0740	.1871	.0754	.0765	.0742
.4625	.0948	.0893	.0982	.0792	.3657	.0853	.0868	.0834
.6623	.1083	.0921	.0982	.0802	.5236	.0913	.0885	.0893
1.021	.0998	.0943	.0999	.0820	.8069	.0957	.0942	.0973
2.172	.1259	.1146	.1186	.1170	1.717	.1063	.1060	.1050
C. Bar 2.8595 cm. diameter ; 91.5 cm. long.					Mean of Reluctances at all Inductions.			
Air-gap in terms of the diameter of the pole-face.	Air-gap Reluctance. Induction-density about 4500.	Air-gap Reluctance. Induction-density about 10000.	Air-gap Reluctance. Induction-density about 16900.		Mean Reluctances of Bar A at distances given in Table A.	Mean Reluctances of Bar B at distances given in Table B.	Mean Reluctances of Bar C at distances given in Table C.	
.1077	.0352	.0310	.0500		.0664	.0633	.0387	
.2399	.0423	.0420	.0591		.084175	.0754	.0478	
.4924	.0536	.0511	.0634		.0904	.0852	.0560	
.9966	.0588	.0585	.0665		.0947	.0897	.0613	
1.5737	.0646	.0676	.0737		.0940	.0957	.0686	
					.1190	.1058		



Fig. 2.  
Reluctance of Air-gaps.



Ordinates : Reluctances  $\times 10^3$ .

Abscissæ : Air-gaps in diameters.

Lettering as in General Table XVII.

§ 19. We can make a comparison between the work done by a ring magnet when it is divided at one point with the work done when the ring is divided at two points. The reluctance data show that though the mean air-gap reluctance may be larger than that of the iron, it is not very greatly so in any practical case, and we can therefore obtain no information by supposing that one is much greater or less than the other; but must proceed by actual trial from the curves to find out which is the most efficient arrangement.

§ 20. In the case of a mechanism represented by a ring divided at one point only, we must remember that the closure of the induction curves involves a "sliding" magnetic contact, and if friction on the bearings is to be avoided this practically ties us down to iron of symmetrical form.

§ 21. Incidentally I had occasion to observe the change of reluctance caused by cutting a bar, and then grinding and polishing the ends. This was not done quite so well as in our most successful attempts. The reluctance corresponded to a separation of the bars by about 20 wave-lengths of sodium light, but I am certain that the bars could not have been half so far apart as this, so the surface reluctance is still unaccounted for.

Sydney, 13th July, 1893.

### VIII. *On a new Harmonic Analyser.*

By Prof. O. HENRICI, *F.R.S.\**

§ 1. **A**CCORDING to the theory of Fourier's Series any function  $y$  of  $x$  can, under certain restrictions, be expanded in a series progressing according to cosines and sines of multiples of  $x$ .

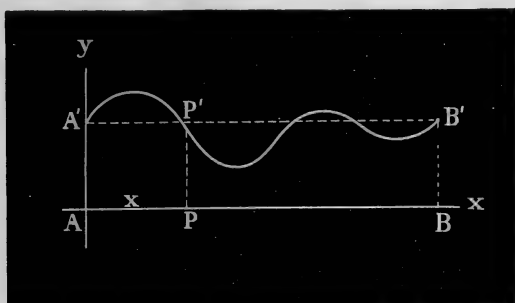
This function may be represented graphically by a curve,  $x$  and  $y$  being taken as rectangular co-ordinates, or it may be defined by aid of such a curve.

Anyhow, we shall suppose this curve given, and also that it extends from  $x=0$  to  $x=c$  (fig. 1). For this interval the curve may be drawn perfectly arbitrary as long as it gives for every  $x$  one single finite value of  $y$ . This implies that if a point moves along the curve the corresponding value of  $x$  always increases. The curve may, however, be discontinuous, so that for a particular value of  $x$  the ordinate changes suddenly from a value  $y_1$  to a value  $y_2$ , as from  $C$  to  $C'$  in

\* Communicated by the Physical Society: read March 9, 1894.

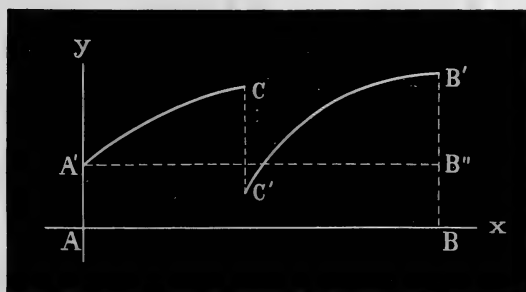
fig. 2. There may be any finite number of such discontinuities. For our purposes it is necessary to make the curve continuous by joining the two points  $C'$  and  $C$  by a straight

Fig. 1.



line. If the curve represents a periodic phenomenon with period  $c$ , then the ordinate for  $x=c$  will, as a rule, equal the initial ordinate for  $x=0$  (as in fig. 1). The curve when repeated along the axis of  $x$  will therefore be continuous.

Fig. 2.



Otherwise there will be a discontinuity as at B in fig. 2. In this case also the curve has to be continued from its end point  $B'$  along the last ordinate to a point  $B''$  which has the same ordinate as the initial point  $A'$ , so that the line  $A'B''$  is parallel to the axis of  $x$ .

We can now express the equation to the curve in the form

of a Fourier Series,

$$y = \frac{1}{2} A_0 + A_1 \cos \theta + A_2 \cos 2\theta + \dots + A_n \cos n\theta + \dots \\ + B_1 \sin \theta + B_2 \sin 2\theta + \dots + B_n \sin n\theta + \dots$$

where  $\theta = \frac{2\pi x}{c}$ .

The absolute term  $\frac{1}{2}A_0$  equals the mean ordinate of the curve, and can therefore be determined by any planimeter. It is the object of the Harmonic Analyser to determine the other coefficients. Their well-known values are

$$A_n = \frac{1}{\pi} \int_0^{2\pi} y \cos n\theta \, d\theta; \quad B_n = \frac{1}{\pi} \int_0^{2\pi} y \sin n\theta \, d\theta.$$

The Analyser is therefore an integrator.

If the paper with the curve be wrapped round a cylinder, the ordinate  $y$  falling on the generating lines or edges, the axis of  $x$  along a circumference, then the curve will run back in itself and form one continuous line, provided the circumference of the cylinder equals the base  $c$ . That edge which passes through the initial point  $A'$  of the original curve may be called the zero-edge.

Suppose the cylinder to lie horizontal with the zero-edge at the top, then our angle  $\theta$  will be the angle through which the cylinder has to be turned in order to bring that point  $P$  to the top which corresponds to any given  $x$ . Each edge contains one point on the curve, excepting in case of a discontinuity where a finite length of the edge belongs to the curve.

§ 2. The first instrument of this kind was constructed by Lord Kelvin (Proceedings Roy. Soc. vol. xxiv., 1876). Since then several others have been devised. With regard to these I may refer to my article "Ueber Instrumente zur harmonischen Analyse" in the Catalogue prepared by Prof. W. Dyck of Munich for the Mathematical Exhibition which was held last summer in Munich, and also to the descriptions in the Catalogue of the various instruments exhibited.

These instruments differ essentially either in the manner in which the trigonometrical factor is introduced, or in the arrangement by which the actual integration is performed. Lord Kelvin uses for the latter purpose his brother's disk-globe and cylinder integrator, whilst a simple harmonic motion introduces the trigonometrical factor. Sommerfeld and Wiechert\* of Königsberg make the cylinder on which

\* See above Catalogue, p. 274.

the curve is drawn rotate about an axis perpendicular to that of the cylinder, and thus avoid the simple harmonic motion, which is always a drawback, as it introduces a great deal of friction. Both instruments are also large and heavy, practically fixtures in the room where they are used.

§3. Clifford has given a beautiful graphical representation of Fourier's Series, which I knew more fully from personal communication than from the short paper published in vol. v. of the Proceedings of the Lond. Math. Soc.

His result may be stated thus:—"If the curve to be analysed be stretched out in the direction of the  $x$  to  $n$  times its base without altering the  $y$ , and then wrapped round a cylinder with circumference  $c$  so that it goes  $n$  times round, then the orthogonal projection of this curve on that meridian plane which passes through the zero-point of the curve will enclose an area which is proportional to the coefficient  $B_n$ . In the same way  $A_n$  is got by aid of a plane perpendicular to the first."

It was this theorem which led me to the construction of an Harmonic Analyser. It can easily be put in the following form. Suppose the cylinder placed with its axis horizontal and the tangent plane to its upper edge drawn. This edge cuts the curve in  $n$  points. Let  $P$  be one of them. If now the cylinder be turned, and if at the same time the tangent plane be moved in its own plane in a direction perpendicular to the edge of contact, the point  $P$  will trace a curve on it. This plane will be the same as Clifford's curve in case the motion of the tangent plane is simply harmonic, completing one period for each rotation of the cylinder. The curve will be completed after  $n$  rotations of the cylinder.

The same curve will be traced if the original, unstretched, curve is wrapped (once) round the cylinder, whilst the tangent plane completes  $n$  periods of its simple harmonic motions for one revolution of the cylinder.

We thus get in a fixed plane a curve whose area equals, in some unit, the coefficients  $A_n$  or  $B_n$ , and this area can be determined by an ordinary planimeter. The curve, of course, need not be drawn out, as long as the tracer of the planimeter is always at the point  $P$  it will describe the curve.

This can easily be realized. A flat board, whose upper surface forms a platform on which the planimeter can rest, is placed by the side of the cylinder so that its upper surface lies in the tangent plane. A straight-edge is fixed above the upper edge of the cylinder. The tracer of the planimeter is pressed against it and made to follow the point  $P$  on the curve. After a complete revolution of the cylinder,

the planimeter will register a number proportional to the coefficient  $A_n$  or  $B_n$ .

I had an instrument of this kind made early in 1889, but it did not turn out quite as simple as its theory. It gives, of course, only one coefficient at a time, though it would not be difficult to construct it to give more terms if it were not for the mechanism required to produce the simple harmonic motion. This always introduces a certain amount of friction if it is to work accurately. I therefore tried to do away with this, and obtained my object in the manner now to be described.

§ 4. If the definite integrals which determine the coefficients  $A_n$  and  $B_n$  be integrated by parts, we get for the former

$$n\pi A_n = [y \sin n\theta]_0^{2\pi} - \int_0^{2\pi} \sin n\theta \, dy,$$

the limits relating to  $\theta$ .

If the original curve is continuous, the integrated part vanishes. This is not the case if there is a discontinuity, at least not if  $\theta$  is retained as the independent variable.

To prove that in this case also the integrated part can be neglected, let us consider the curve in fig. 2. Let  $\theta'$  be the value of  $\theta$  for which the discontinuity  $CC'$  occurs, and let  $y_1'$  be the ordinate of  $C$ , and  $y_2'$  that of  $C'$ .

The integral with regard to  $\theta$  has to be broken up into two, the first going from 0 to  $\theta'$ , the second from  $\theta'$  to  $2\pi$ . The integrated part, therefore, gives

$$y_1' \sin n\theta' - y_2' \sin n\theta',$$

and this, in general, does not vanish.

The remaining integral has to be taken for the two parts of the curve from  $A'$  to  $C$  and from  $C'$  to  $B'$ , if the curve is not made continuous. But if the curve is made continuous, we have also to take the integral for the intervals from  $C$  to  $C'$ , and from  $B'$  to  $B''$ . For these  $d\theta$  vanishes, but not  $dy$ . This gives in addition the integrals

$$-\int_C^{C'} \sin n\theta \, dy = -\sin n\theta' \int_C^{C'} dy = -\sin n\theta' (y_2' - y_1');$$

hence just the terms obtained before from the integrated part.

The second integral for the interval  $B'B''$  vanishes because it is multiplied by  $\sin 2n\pi$ . In case of the coefficient  $B_n$  this is not the case, but then the integrated part also contains more terms which equal it. Hence:—

*If the integration is performed with regard to  $y$  we get*

$$n A_n = \frac{-1}{\pi} \int \sin n\theta \, dy, \quad n B_n = \frac{1}{\pi} \int \cos n\theta \, dy,$$

*both taken over the whole continuous curve from  $A'$  to  $B''$ . If the integration be continued from  $B''$  to  $A'$  on the line parallel to the axis of  $x$  nothing is added to the integral, because here  $dy$  vanishes.*

For the Analysers now to be described this extension of the integration should always be made in order to eliminate certain errors of the instrument.

These new integrals are of a very different form from the old ones, and require accordingly a different mechanism. As the tracer of the instrument follows the curve, each  $dy$  has to be multiplied by  $\sin n\theta$  or  $\cos n\theta$ . In other words, we have to decompose the  $dy$  for each element of the curve into two components at right angles to each other, of which the one makes an angle  $\theta$  with the axis of  $x$ , and then add all components of each kind to get  $A_n$  and  $B_n$ .

Originally I did this by aid of a pair of registering-wheels such as are used in Amsler's well-known planimeter, the axes of the two being at right angles. If such a wheel moves along a straight line of length  $p$ , making an angle  $n\theta$  with its own axis, it will register not  $p$  but  $p \cos n\theta$ , whilst the second wheel at right angles to it gives  $p \sin n\theta$ .

A model of this instrument was made in 1889.

The curve is wrapped round a horizontal cylinder. Parallel to this a carriage runs on a rail carrying the tracer which moves along the upper edge of the cylinder. It also carries a vertical spindle which has the two registering-wheels attached to it. These roll on a horizontal platform. If, now, this spindle is made to turn through an angle  $n\theta$  when the cylinder has turned through an angle  $\theta$ , and if the tracer is made to follow the curve, then the two registering-wheels will give the coefficients  $A_n$  and  $B_n$ . For the details of the construction I must refer to Prof. Dyck's Catalogue, p. 213.

§ 5. The next improvement is due to Mr. A. Sharp, of the Teaching Staff in the Guilds' Central Technical College. Having used my model, he brought me a design in which the principles explained were realized in a different manner. Among the alterations introduced one struck me as being of importance. It consisted in an inversion of the motion, the curve being drawn on the drawing-board and the instrument made to move over it whilst the registering-wheels rolled on the paper.

It seemed to me that we had now all the elements needed

for a really good instrument, and only wanted a practised instrument-maker to realize it. I therefore called in 1892 on Coradi in Zürich, well known for his planimeters and integrators. He set to work at once and sent me in a short time a drawing of his construction, and it is due to his skill that the instrument has, at last, reached a high degree of perfection. One Analyser has been made for the Guilds' Central Technical College, which I shall describe. But I must mention at once that Herr Coradi has since greatly improved it, so much so that it is now one of the most perfect integrators made.

§ 6. Fig. 3 shows an instrument of Coradi's second design. This will help to explain the first.

There is first of all a solid frame whose base is a long rectangle. It rests with three wheels on the drawing-board. One of these, D, in the middle of the front, serves merely as a support. The other two, E, E, are fixed to the ends of a long axle which runs along the back of the frame. This may be called the "shaft." It is placed parallel to the axis of  $x$ . The instrument can, therefore, roll over the paper in the direction of the ordinates  $y$ .

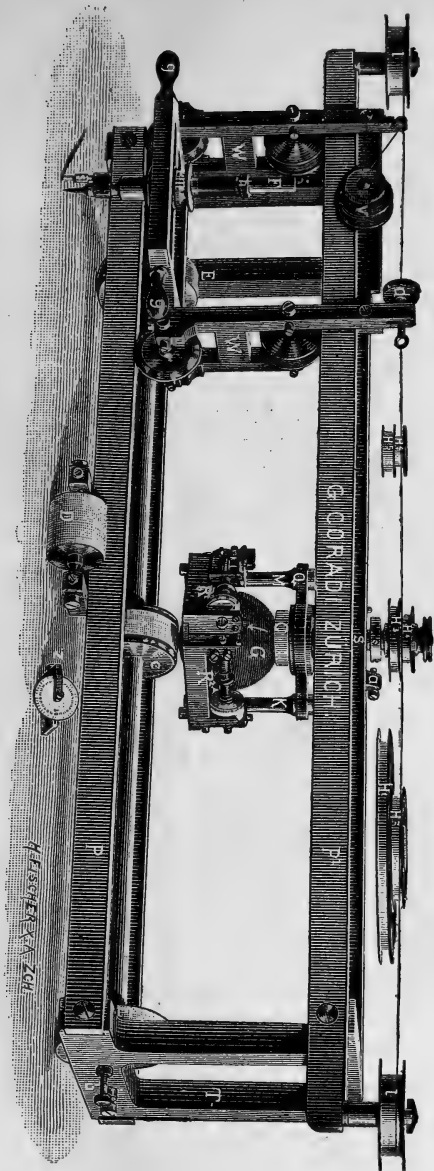
If thus moved through a distance  $dy$ , the shaft will turn through an angle proportional to  $dy$ . The shaft carries any required number of short "cylinders." In the figure there is one marked C situated in the middle of the shaft.

Above each of these cylinders is a vertical "spindle" S, whose geometrical axis cuts that of the shaft. In the new instrument each spindle carries one or two disks,  $H_3$ ,  $H_4$ , in fig. 3; but in the old construction one crown wheel with its teeth pointing upwards, by aid of which the spindle is turned. At the lower end the integrating apparatus proper is attached, which is quite different in the two designs. But before explaining this let me describe how the spindle is turned.

Along the front of the frame runs a carriage W, to which the tracer F is fixed. This can be moved through a distance equal to the base  $c$  to which the curve is drawn. To the carriage a silver wire is also attached, which in the new design is stretched along the front of the frame and then by aid of guide-pulleys  $l, l$  over one of the disks H on top of the spindle S (see fig. 3). By giving the disk H a suitable diameter the spindle can be made to turn  $n$  times round, whilst the tracer describes the whole base. In the old instrument the wire only drives an extra spindle in the middle of the frame, which by aid of wheelwork drives all the working spindles. If the tracer on following the curve has reached a



Fig. 3.



point P, then the spindle will have turned through an angle  $n\theta$ , where  $\theta$  corresponds to the  $x$  of P.

If, now, the spindle had at its lower end two registering-wheels at right angles to each other rolling on the drawing-paper, we should have in principle my old model (§ 4) with Sharp's inversion. Instead of this Coradi gave each spindle one registering-wheel and made this roll on the cylinder C. This requires for each registering-wheel a separate spindle, hence two for each pair of coefficients  $A_n$  and  $B_n$ . It substitutes, however, the rolling on a smooth surface for that on the rough surface of the paper. The instrument made according to this design for the Guilds' Central Technical College has five such pairs, so that on going once over the curve the first five pairs  $A_n$  and  $B_n$  are obtained. The extra spindle which is driven by the silver wire contains, however, three extra disks, making four in all. If the wire is stretched over the top disk we get, as stated, the coefficients for  $n=1, 2, 3, 4, 5$ . The second pulley has half the diameter, so that the spindles turn twice as fast if the wire is stretched round it. Thus in going over the curve a second time we get the new coefficients for  $n=6, 8, 10$ . The remaining two disks give similarly the coefficients for  $n=7$  and  $9$  respectively. Hence on going four times over the curve we get ten pairs of coefficients. In most cases the five pairs obtained at once will be amply sufficient.

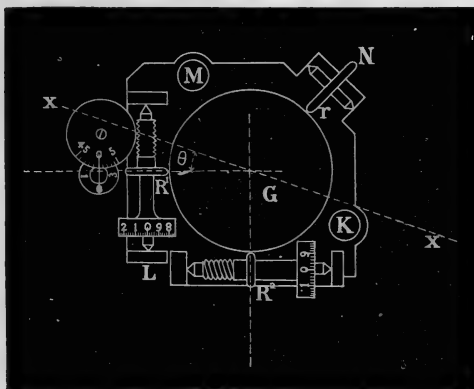
For the details of the construction I must again refer to Prof. Dyck's Catalogue (*Nachtrag*, p. 34) and only mention a few points. The axis of a registering-wheel lies in the diameter of a horizontal ring which is attached to the lower end of the spindle by aid of an elastic vertical steel plate. This presses the wheel against the cylinder, securing contact. On testing the instrument it was found that this plate was liable to slight torsion which affected the readings. It showed a number of other drawbacks of more or less importance. One is that the registering-wheel not only rolls but also slips. This slipping is absent in the Analyser of Lord Kelvin, who has dwelt strongly on the importance of avoiding it.

There was also a serious difficulty in taking the readings. The instrument registers up to 20 centim. If the zero-point has passed the index which gives the reading, 20 centim. have to be added or subtracted. Every one who has used a planimeter is accustomed to this, and knows how to take account of it, for he can either estimate the area sufficiently to see which correction is necessary, or he can go rapidly over the curve again, watching the zero-point. Neither method is possible with an Analyser which gives a large

number of readings at once. The new instrument is therefore constructed to record up to 200 centim.

§ 7. Last summer at the Munich Exhibition Herr Coradi submitted a new arrangement to me to obviate some of the imperfections of the instrument described, and this he has since carried out with an ingenuity which I cannot enough admire. He has practically got rid of all the imperfections of the old Analyser, and has now produced an instrument which, I fancy, leaves nothing to be desired. He himself says it is the best instrument of any kind he has yet made. The chief alteration is this, that he interposes between the registering-wheel at the lower end of the spindle and the cylinder a perfectly free glass sphere.

Fig. 4.



The "spindle" has now *firmly* attached to its lower end a square frame K L M N (comp. figs. 3 and 4) by aid of two solid rods K and M, instead of carrying the ring connected by aid of an elastic spring. This frame holds two registering-wheels  $R^1$  and  $R^2$ , whose axes K L and L M are at right angles. Between these lies the glass sphere G, resting with its lowest point on the cylinder belonging to the spindle. A third wheel  $r$  at N is by aid of a spring pressed against the sphere to secure contact between the latter and the registering-wheels. If, now, the tracer follows the curve this frame will turn with the spindle, the three wheels will carry the sphere with it, which will turn pivot-like on its lowest point. If, as in fig. 4, the plane of one wheel  $R^1$  makes with the axis of  $x$  an angle  $n\theta$ , and if in this position the tracer, and with it the whole instrument, is moved through the distance  $dy$ , the "shaft" will turn proportionally to  $dy$ . This will set the sphere turning about its horizontal diameter  $xx$  parallel to the

shaft, and this motion will be communicated to each of the registering-wheels. It will be seen at once, if  $q$  denotes the radius of the sphere, the point of contact of the sphere and the wheel  $R^1$  is at a distance  $q \sin n\theta$  from the axis of the sphere, that therefore the turning communicated to this wheel will be proportional to  $dy \sin n\theta$ . Similarly the other wheel will turn proportionally to  $dy \cos n\theta$ . If the tracer moves through the whole curve, these two wheels will therefore register numbers proportional to  $A_n$  and  $B_n$ . The dimensions are so chosen that the readings give  $nA_n$  and  $nB_n$  in centimetres.

It will be seen that now one spindle does the work of two in the old instrument. There is, further, no slipping of any kind in the integrating apparatus.

Another improvement is that the wheelwork for turning the spindles is done away with. Each spindle is turned directly by the silver wire, and thus any slackness in the wheels is done away with.

It has also been possible to introduce an arrangement to set all spindles to zero after the wire has been tightened.

Lastly, the readings are taken with much greater ease as the registering apparatus is well exposed to the eye.

In order that the instrument may work accurately it is necessary that the point of contact of the sphere with its cylinder should lie in the geometrical axis of the spindle. But it is practically impossible to secure this. This point will therefore describe a small circle on the cylinder and this will turn the sphere about some horizontal diameter, and therefore also the registering-wheels. It is of importance to eliminate the error thus introduced. This is done by bringing the tracer back to the starting-point  $A$  on the curve by moving it from  $B$  to  $A$  (figs. 1, 2) parallel to the axis of  $x$ . The sphere will hereby repeat the motion which produced the error, but in the opposite sense, and therefore completely cancel it.

§ 8. The first instrument of this kind has been made for Prof. Klein at Göttingen. It contains one spindle, as in fig. 3. Going once over the curves it gives therefore one pair of coefficients. To get more, disks of different diameter have to be used to drive the spindle. Of these six are provided. Since then two further instruments have been finished; one with five spindles, which goes to Moscow, the other, with three spindles, for Prof. Weber in Zürich. The experience gained in the making of the Göttingen instrument has enabled Coradi to introduce a number of small improvements, with the result that the carriage runs in the Moscow instrument, where it has to drive five spindles, as easily as in the one for Göttingen with only one spindle.

He has also introduced a celluloid ring below the sphere, which on being raised presses the sphere against a similar ring above, thus preventing any damage to the integrating apparatus when the instrument is not being used.

*Note.*—At the request of Herr Coradi I add the statement that the idea of the new integrating apparatus, consisting of a sphere with two recording-wheels at right angles to each other, is not his own, but is due to Herr Max Küntzel, of Charlottenhof, near Königshütte in Silesia. Herr Küntzel invented the arrangement for an instrument designed to determine the coordinates of the vertices of a polygon, and submitted his design to Herr Coradi for the construction of such an instrument.

IX. *Harmonic Analyser, giving Direct Readings of the Amplitude and Epoch of the various constituent Simple Harmonic Terms.* By ARCHIBALD SHARP, B.Sc., Wh.Sc., A.M.I.C.E.\*

LET the curve (fig. 1) be that represented by the equation  $y=f(x)$ , the scale of abscissæ being such that the period is  $2\pi$ . Suppose a wheel W to roll on the paper

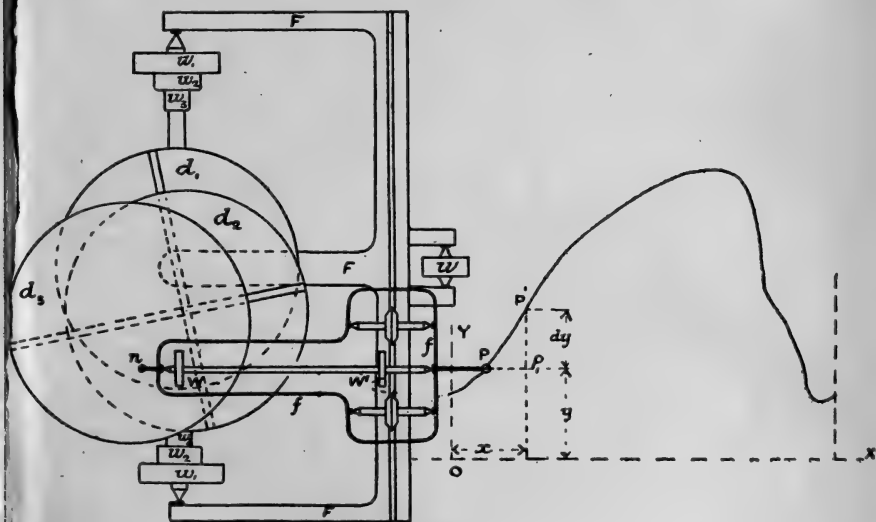


FIG. 1

(fig. 2), and to be connected with a tracing-point P (fig. 1) in such a manner that as P moves uniformly in the direction

\* Communicated by the Physical Society: read April 13, 1894.



In the Fourier expansion

$$y=f(x)=A_0+A_1 \sin x+A_2 \sin 2x+\ldots+A_n \sin nx+\left. \begin{aligned} &+B_1 \cos x+B_2 \cos 2x+\ldots+B_n \cos nx+\ldots \end{aligned} \right\} (1)$$

$$\left. \begin{aligned} A_1 &= \frac{1}{\pi} \int_0^{2\pi} y \sin x dx = \frac{1}{\pi} \int \cos x dy = -\frac{1}{\pi} \text{OR}' \\ B_1 &= \frac{1}{\pi} \int_0^{2\pi} y \cos x dx = \frac{1}{\pi} \int \sin x dy = -\frac{1}{\pi} \text{RR}' \end{aligned} \right\} \quad (2)$$

Also  $f(x)$  may be expanded in the form

$$A_0+C_1 \sin (x-\alpha_1)+C_2 \sin (2x-\alpha_2)+\ldots C_n \sin (nx-\alpha_n), \quad (3)$$

$A_n, B_n, C_n$ , and  $\alpha_n$  being connected by the relations

$$\left. \begin{aligned} A_n &= C_n \cos \alpha_n \\ -B_n &= C_n \sin \alpha_n \end{aligned} \right\}, \quad \cdot \cdot \cdot \quad (4a)$$

or

$$\left. \begin{aligned} C_n^2 &= A_n^2 + B_n^2 \\ \tan \alpha &= -\frac{B}{A} \end{aligned} \right\} \quad \cdot \cdot \cdot \quad (4b)$$

From (2) and (4b) it is evident that OR (fig. 2) is equal to  $\pi C_1$ , and the angle Y'OR is equal to  $\alpha_1$ .

If now the axis of the rolling wheel W makes  $n$  turns while the tracer P moves over one complete period of the curve (fig. 1), the corresponding values of OR and the angle Y'OR will be  $n\pi C_n$  and  $\alpha_n$  respectively.

Various arrangements of mechanism are suggested for connecting the rolling wheel with the tracer so as to satisfy the above conditions; the following seems the most suitable, as it can be adapted for an instrument to give more than one simple harmonic constituent term for one tracing of the curve.

The motion of the rolling wheel relative to the paper is compounded of two simple movements:—(a) a pure rolling, the distance rolled being equal to  $dy$  the element described by the tracer P; (b) a motion of rotation, the point of contact of the wheel with the paper being the centre of rotation, and the angle turned through from the initial line being proportional to  $x$  the abscissa of P. The relative motion will, therefore, be the same if the wheel be rolled along a straight line *fixed* in the instrument, while the *paper* is made to turn, the centre of rotation of the paper being the point of contact of the wheel with it which is continually varying in position. Fig. 1 represents diagrammatically the mechanism. The curve

to be analysed is drawn on a flat sheet of paper and placed on a drawing-board. The carriage FF, which forms the base of the instrument, is supported by an axle with two equal wheels  $w_1$  and a third wheel  $w$  which roll on the paper, the direction of motion of the carriage being OX. A disk  $d_1$  mounted on a vertical spindle is driven by a pair of bevel wheels by the axle  $w_1 w_1$ . A long key on the upper surface of this disk fits into a groove on the under surface of a disk  $d_2$ , which is thus free to move in a straight line relative to disk  $d_1$ . A groove on the upper surface of disk  $d_2$  at right angles to that on its lower surface has a key from the lower surface of disk  $d_3$  resting in it. Thus the disk  $d_3$  always turns with disk  $d_1$ , although any point on disk  $d_3$  may be made the centre of rotation; the three disks being kinematically equivalent to Oldham's coupling for the transmission of motion between two parallel shafts. The keys and grooves would be replaced, in an actual instrument, by wheels and rails, in order to diminish frictional resistance.

The tracing-point P is mounted on a smaller carriage  $f$ , which is free to run in the direction OY relative to the main carriage F. This smaller carriage carries also the rolling wheel W which rolls on the disk  $d_3$ . The rolling wheel W should be spherical in form, and of as small diameter as possible, so that its surface of contact with the paper on disk  $d_3$  approximates to a point. The friction between wheel W and disk  $d_3$  is great enough to prevent any relative sliding. As the tracer P moves over the curve (fig. 1) the point of the wheel W will describe on the disk  $d_3$  the curve Opp'R (fig. 2). To ensure that, as the tracer P is moved in the direction OY, the wheel W will *roll* on the disk  $d_3$  the same distance and not displace it relative to disk  $d_1$ , a wheel W' of the same diameter as W is mounted on the same spindle and rolls on a fixed portion of the carriage FF. If W' be compelled to roll, W must roll on the disk  $d_3$  an equal amount.

The actual shape of the curve Opp'R (fig. 2) is of no importance, the initial and final points being all that are required. A needle or pencil  $n$  may therefore be carried at any convenient part of the carriage  $f$ , and the initial and final positions O and R marked by it. The direction of the initial line OR will be recorded on the disk  $d_3$  by making two marks with the needle  $n$  as the tracer P moves along the line OY (fig. 1).

The gearing must be such that the disk  $d_3$  turns once while the tracer P describes one complete period of the curve. If now pairs of equal wheels  $w_2 w_2, w_3 w_3, \dots$  of diameters



$\frac{1}{2}, \frac{1}{3}, \dots$  of  $w_1$ , be made to roll on flat rails lying on the paper, the values of  $c_2, a_2, c_3, a_3, \dots$  are obtained in succession, one pair of coefficients for each tracing of the curve.

This instrument has the advantage over any Harmonic Analyser previously designed that it gives directly the quantities—amplitude and epoch—of each simple harmonic term which are required; all other instruments, as far as I am aware, giving the coefficients  $A_n$  and  $B_n$ , from which  $C_n$  and  $a_n$  are calculated.

It is remarkable that no adjustments have to be made before using the instrument, the initial position of the disk  $d_3$  having no influence on the curve  $Opp'R$  described on it. There is no part of the instrument which demands *excessive* accuracy of construction. The accuracy and delicacy of the instrument depends on the accuracy with which the line OR and angle  $Y'OR$  can be measured, and will be quite as great as that with which the original curve fig. 1 is drawn.

In some cases there will be a danger that the disk  $d_3$  may not be large enough to contain the complete curve  $Opp'R$  (fig. 2). If the rolling wheel W is about to roll off the disk, a mark should be made with the needle  $n$ , and keeping the tracer P in the same position, the disk  $d_3$  should be moved by hand into any other convenient position relative to disk  $d_1$ , a new mark made with the needle, and the movement of the tracer P may then be proceeded with. The final line OR can then be easily built up from its separate parts.

Since writing the above I have designed an inversion of the mechanism described above giving a simple compact instrument, which I may have the pleasure of describing later on.

X. *Remarks on Prof. Henrici's Paper made by Prof. PERRY, F.R.S., in which he describes a Simple Machine which may be used to develop any Arbitrary Function in Series of Functions of any Normal Forms\*.*

**I** CONGRATULATE Prof. Henrici, first upon his success in these Analysers, with which I shall presently form a practical acquaintance when the latest of them yet constructed reaches me from Zurich, second on the admirably clear way in which he described them to us.

I have had no experience with the hatchet, that simplest of all planimeters; but with regard to the Robertson-Hyne

\* Communicated by the Physical Society: read April 13, 1894.

instrument, which comes to us from America, and which in the size here exhibited is well suited to Indicator-diagram work, I can say that some of my students instituted a careful comparison between it and the Amsler which they use for Indicator diagrams, and they found that the average error with it was about one third of that with the Amsler.

We know that in mathematical physics generally the development of an arbitrary function in a Fourier's Series is often of great importance; but I wish to say that this subject is becoming of greater and greater importance to the practical man—the engineer.

Thus in alternating-electric-current work, all the disturbing, distracting, dangerous troubles are considerably increased when the currents are not simple harmonic functions of the time. With two-phase or three-phase currents, if the amplitudes are not equal, the rotating magnetic field neither remains of constant strength nor has it constant angular velocity; and if there are overtones we have extra fields of changing magnitude, which rotate irregularly at two or more times the speed of the fundamental.

I have long thought that mechanical engineers need such instruments as Prof. Henrici has designed, if only to familiarize them with the ideas of Fourier. It has for some time been my habit, when studying with students any kind of reciprocating motion of a piece of machinery, to resolve the motion into its fundamental harmonic motion and overtones. For example, if one is studying the forces causing the motion, one ought to keep in mind that the reciprocating motion which (speaking rather vaguely) requires the smallest forces or moments of forces to produce it, is the simple harmonic motion. The accelerating forces due to an octave are four times as great as for a fundamental of the same amplitude. The motion of the piston of a steam-engine is, with sufficient exactness for practical calculations, a fundamental of amplitude  $r$  and an octave of amplitude  $\frac{r^2}{4l}$ , where  $r$  is the length of the crank and  $l$  the length of connecting-rod.

A special graphical method of study may be discovered and employed for any special motion; but for applicability to reciprocating motions in general I know of nothing to compare with the method of study which is based on finding the fundamental motion and one or more overtones.

Again, the difference between one kind of slide-valve motion and another may be exceedingly great, practically, and yet the theories found in books show no difference at all. Indeed, the complete mathematical methods of study are too

troublesome, but the mathematics of link motions and radial valve-gears become very simple when we consider, not merely the fundamental simple harmonic motion, which is all that is usually studied, but the octave, which is found to help or hurt in the various forms.

I was first attracted to this subject when studying the beautiful but little-known valve-motion invented long ago by Sir F. Bramwell, in which the only overtone is three times the fundamental.

Given any function completely, we can by a numerical method, and with as much accuracy as we please, develop it in Fourier's Series. In the 'Electrician' of Feb. 5th, 1892, I published the numerical work of one example calculating from 23 ordinates. In the sheet which I here exhibit one of my students, Mr. Fox, has done the same work by a graphical method. Probably he is the very first to carry out the idea of the late Prof. Clifford by descriptive geometry\*. That is, we have imagined the curve to be wrapped round the cylinder, and it was surprising to find how rapidly its projections could be drawn upon the two planes and their areas obtained by the planimeter. We then imagined the curve to be wrapped twice round and the projections drawn and their areas taken. I wish I had time to dwell upon the interesting problems that arose during the work, for example as to whether the area was to be taken as positive or negative. However many loops such a figure may possess, the well-known rule for autotomic plane circuits (Thomson and Tait's 'Elements,' §445) is really attended to by the planimeter. The direction of motion of

\* *Note added May 29th.*—The descriptive geometry method is fairly quick, and may be made as accurate as one pleases, but of course it cannot compare in quickness with the Henrici Analyser.

It is obvious that by properly shaping one's cylinder, wrapping the curve round it, and then finding the area of it, projected on a plane parallel to the axis, one may develop an arbitrary function in a series of any normal forms. Thus if  $Q(x)$  is any tabulated function of  $x$ , and  $y$  is the arbitrary function of  $x$ , and we wish to find the integral  $\int_0^a y \cdot Q(x) \cdot dx$ , the shape of the curve which must be used instead of a circle in the Clifford construction is easy to find. It must be such that the cosine of the angle which the short length  $\delta x$  of the curve makes with the trace of the plane on which the projection is to take place shall be proportional to  $Q(x)$ , and several easy methods of drawing the curve or a series of such curves may be found. Once found, there is no more difficulty in developing any new arbitrary function in any series of normal forms than Mr. Fox found with his Fourier Series. A series of curves will be needed for a development in Zonal Harmonies, but only one curve will be needed for the Zeroth Bessels. These curves, or shapes of sections of cylinders, I am now proceeding to draw on a sufficiently large scale for exact work.

the tracer must be that in which  $x$  increases on the real curve. I here give the results :—

The values of the arbitrary function to be analysed were really calculated from

$$y = 10 + 5 \sin \left( \frac{2\pi}{c}x + 30^\circ \right) - \sin \left( \frac{4\pi}{c}x - 60^\circ \right).$$

The result obtained numerically and published in the 'Electrician,' using 23 ordinates, was

$$y = 9.966 + 5.039 \sin \left( \frac{2\pi}{c}x + 29^\circ.9 \right) - 1.053 \sin \left( \frac{4\pi}{c}x - 55^\circ.3 \right).$$

The result now obtained graphically is

$$y = 10.01 + 5.0096 \sin \left( \frac{2\pi}{c}x + 30^\circ.38 \right) - 1.0099 \sin \left( \frac{4\pi}{c}x - 59^\circ.2 \right).$$

It is curious that Prof. Henrici should have based the construction of his first or 1889 instrument on the beautiful idea of the late Prof. Clifford, and not on what I call the Henrici principle. He gives the Henrici principle to explain the later instruments, and does not seem to see that his first instrument is the most beautiful example of its application. I take the Henrici principle to be that  $\int y \cdot \sin \theta \cdot d\theta = \int \cos \theta \cdot dy$ , the integrations being for a whole period. Well, in his first instrument, whilst its tracer moves through the distance  $dy$ , the ordinarily fixed part of the planimeter now has a displacement  $\cos \theta$ , and this is the same as if in the ordinary use of the instrument a curve is being traced whose ordinate is  $\cos \theta$ .

It is only on the assumption that the Henrici principle applies to his first instrument, that I venture to say that the following analyser is on the Henrici principle. We have at present to develop functions in sines and cosines, spherical harmonics and Bessel functions, because we know that when we have effected such developments we can convert them at once into the solutions of certain physical problems. As time goes on we shall require developments in many other normal forms. I propose to describe a machine which will effect any such development. I mean, that my machine will

evaluate the integral  $\int_0^a f(x) \cdot Q(x) \cdot dx$ , where  $y=f(x)$  is an arbitrary function of  $x$  and  $Q(x)$  is any tabulated function. Following Henrici, we convert the required integral into

$$\left[ \int_0^a f(x) \cdot H(x) \right] - \int H(x) \cdot dy,$$

where  $H(x)$  is the integral of  $Q(x)$  and may be tabulated as  $Q(x)$  is tabulated. Now in many cases the part between the square brackets is zero, but this is of little consequence in comparison with the fact that the part  $\int H(x) \cdot dy$  may be evaluated by a machine somewhat like Prof. Henrici's first or 1889 instrument. I have worked with this 1889 instrument, and I am not disposed to think it so inaccurate as its inventor thinks it. Its defects are really defects of mechanical construction; for example, the amplitude of the simple harmonic motion of its table is very much too small.

I have already put my machine in hand and hoped to exhibit it here to-day in working order, but unfortunately the Easter holidays have prevented it being finished in time. It is arranged to develop an arbitrary function in Bessels of the zeroth order, or rather Fourier cylindric functions. Thus it is required to determine the constants  $A_1, A_2, \&c.$ , in

$$f(r) = A_1 J_0(\mu_1 r) + A_2 J_0(\mu_2 r) + \&c., \quad . \quad . \quad . \quad (1)$$

where  $\mu_1, \mu_2, \&c.$  are the successive roots of some such equation as

$$J_0(\mu a) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$\mu a J_1(\mu a) - \lambda J_0(\mu a) = 0, \quad . \quad . \quad . \quad . \quad (3)$$

where  $\lambda$  has a given value.

It is well known that

$$A_s = M \int_0^a r f(r) \cdot J_0(\mu_s r) \cdot dr,$$

where  $M = 2/a^2 [J_1(\mu_s a)]^2$ , if  $\mu_1, \mu_2, \&c.$  are the roots of (2), and

$M = 2\mu_s^2/(\lambda^2 + \mu_s^2 a^2) [J_0(\mu_s a)]^2$ , if  $\mu_1, \mu_2, \&c.$  are the roots of (3).

In every case the practical difficulty consists in finding the integral. I exhibit to the Society an easy example of such an analysis worked out numerically (I suppose that such a thing has never been done before) by two of my students, Mr. H. F. Hunt and Mr. W. Fennell.

It will be seen that the work is rather tedious. It was made more tedious by their having found it necessary to calculate numbers and tabulate them in a handy form, interpolating between the numbers given in Lommel by the use of his formula. Before this work was finished we discovered Dr. Meissel's elaborate tables, from which the remainder of our handy four-figure tables is merely copied. These handy tables of  $J_0(x)$  and  $J_1(x)$  are at the service of the Society; they would occupy just four pages of the

Journal. We have found them of practical value, but I do not know whether they are of such general value that they ought to be printed.

It is well known that  $\int_0^x x J_0(x) \cdot dx = x J_1(x)$ , and hence if we write  $\phi(r)$  for  $\mu r J_1(\mu r)$ , and  $y$  for our arbitrary function  $f(r)$ , the required integral  $\int_0^a r f(r) \cdot J_0(\mu r) \cdot dr$  is

$$\frac{1}{\mu^2} \int_0^a y \cdot \frac{d\phi(r)}{dr} dr = \left[ \frac{1}{\mu^2} f(r) \phi(r) \right] - \frac{1}{\mu^2} \int \phi(r) \cdot dy.$$

The part between the square brackets is usually 0, but however that may be, we see that we can evaluate the integral by the machine. A curve is drawn representing  $f(r)$  from  $r=0$  to  $r=a$  on a sheet of paper which is wrapped round a roller.  $a$  need not be equal to the whole circumference of the roller and the scale of  $r$  is unimportant. Of course the ordinate  $y$  or  $f(r)$  lies parallel to the axis of the roller. It is the measurement of  $y$  in inches which my instrument analyses, as my planimeter is graduated in square inches. A table whose upper surface is in a plane tangential to the roller carries the usually fixed part and rolling wheel of an Amsler planimeter. On turning through an angle  $\theta$  of a handle which drives a shaft on which a properly shaped cam is keyed, the table is displaced in its own plane towards the roller, through the distance  $x J_1(x)$ ,  $\theta$  being proportional to  $x$ , and at the same time the roller is driven so that the paper moves circumferentially through a distance proportional to  $x$ . For this particular kind of problem a few different but definite trains of gearing might be used to connect the handle and the roller, but for general purposes I would prefer variable friction gearing to give any relative speeds that may be necessary. In my model now being constructed I am using two disks, one of which rests on the other at a point which may be altered, radially. As in Prof. Henrici's instrument, the tracing-point of the planimeter is held against a straight edge, so that it can only move along the tangent-line of roller and table whilst following the curve on the roller.

If  $\mu$  is a root of  $J_0(\mu a) = 0$  as in the well-known drum-head problem,  $a$  being the radius of the drum-head,—in the first operation to find  $A_1$ , the gearing must be adjusted so that when the whole curve on the roller passes under the tracing-point of the planimeter, a graduated circle on the

shaft turned by the handle indicates that it has turned through an angle proportional to  $2\cdot405$ , which is the first value of  $x$  which satisfies  $J_0(x) = 0$ .

It is advisable to have a pointer and a scale to indicate exactly the displacement of the table, so as to test the accuracy with which the cam performs its duties. Of course, when the graduated-circle indication is  $2\cdot405$ , the displacement of the table is to be  $2\cdot405 J_1(2\cdot405)$  or  $-1\cdot249$  inches. The area recorded on the planimeter in square inches must now be multiplied by  $2(2\cdot405)^2/a^4 [J_1(2\cdot405)]^2$ , and the answer is  $A_1$ .

To find  $A_2$ : change the gearing so that when the whole roller-curve passes under the tracing-point of the planimeter, the graduated circle indicates  $5\cdot5201$ , and check the error of the cam by noting that the displacement indication ought now to be  $5\cdot5201 J_1(5\cdot5201)$  or  $1\cdot878$  inches. The area recorded by the planimeter in square inches must now be multiplied by  $2(5\cdot5201)^2/a^4 [J_1(5\cdot5201)]^2$ . If variable frictional gearing is used, it is important that the roller should be placed on roller bearings of small resistance.

To develop an arbitrary function in Bessels of any other order, or in Fourier's Series, or in zonal harmonics, or in series of functions of any other normal forms, we have only to replace the cam by one of another shape; so that this one simple machine is suited to quite general analytical use.

XI. *On the Effect of Sphericity in Calculating the Position of a Level of no Strain within a Solid Earth, and on the Contraction Theory of Mountains.* By REV. O. FISHER, M.A., F.G.S.\*

I HAVE been permitted to reply to Professor Blake's criticism upon my investigations concerning the relative structure of the continental and suboceanic crust†, and I now hope to do the same to his objections to the calculation of the depth of the "level of no strain"‡—a subject which he admits to be important.

Mr. Blake says that he is surprised that the superficial position of the level of no strain at no more than four miles from the surface "should not be regarded as a *reductio ad absurdum* that the method or premisses which lead to it must be wrong, both *a priori*, that any critical change in condition

\* Communicated by the Author.

† Phil. Mag. vol. xxxvii. p. 375, April 1894.

‡ 'Annals of British Geology,' 1892, p. iv.

could be demonstrable at so insignificant a depth, and *a posteriori*, considering the magnitude of the actually observed features of the earth's surface."

As regards the *a priori* objection, that it is improbable that any critical change in condition should be demonstrable at the small depth of from two to four miles, it may be replied that no claim is made that such a change in condition exists at that depth in the actual earth. But what has been demonstrated is, that, if the earth had cooled as a solid globe, a level of no strain would be found in that position. In that case, however, the surface-features would not have resembled in size and arrangement those which we see. Consequently we *do* regard the improbability of a critical change at so small a depth to be a *reductio ad absurdum*, and conclude that one of the premisses, viz. that of solidity, is wrong. The *a posteriori* objection involves a *petitio principii*; for it assumes that the observed features are due to contraction through cooling, which is the very question that is being brought to the proof.

But it is in the method of investigation rather than in the premisses that Mr. Blake appears to think a mistake has been made; for he contends that the use of the "*linear*"\* equations for the conduction of heat in the calculation of the position of the level of no strain, as was done by Mr. Davison and Professor Darwin †, and also by me, is inconsistent with the introduction of the radius of the earth already assumed infinite. The objection is *primâ facie* plausible, and it had occurred to me; but seeing that the changes of temperature involved occurred only near the surface, I did not think it necessary to take sphericity into account as regarded the temperature gradient; and what follows will show that I was justified. Using for convenience of reference the same symbols as in my book ‡:—

$r$  = the radius of the earth considered spherical, 20,902,404 feet, 3958·78 miles;

$t$  = the time since the globe solidified;

$V$  = the temperature of solidification;

$x$  = the distance of a spherical shell from the surface;

$z$  = distance of the same from the centre;

$v$  = the temperature of that shell when sphericity is neglected—as was done in the work referred to;

\* Mr. Blake thus refers to the equation for the conduction of heat in one dimension.

† Phil. Trans. Roy. Soc. vol. clxxviii., 1887.

‡ 'Physics of the Earth's Crust,' chap. viii., "On the Cooling of a Solid Earth," 2nd ed., 1889, p. 94.



$u$  = the like when sphericity is taken account of ;

$e$  = the coefficient of linear contraction of those portions of the globe which have sensibly cooled ;

$\kappa$  = the conductivity measured in terms of the capacity of rock for heat ;

then the differential equation for the diffusion of heat in the sphere will be

$$\frac{d(zu)}{dt} = \kappa \frac{d^2(zu)}{dz^2}.$$

Professor R. S. Woodward, U.S.A., gives the solution of this, which is suitable to the case of a sphere initially at a uniform temperature throughout, and cooling into a medium such that its surface is maintained at a constant temperature considered to be zero. The solution is \*

$$zu = \frac{2rV}{\pi} \sum_{n=1}^{n=\infty} \frac{(-1)^{n+1}}{n} \epsilon^{-\kappa \left(\frac{n\pi}{r}\right)^2 t} \sin n\pi \frac{z}{r}.$$

This solution meets the objections raised by Professor Blake to Lord Kelvin's solution, in which the radius was assumed infinite.

Prof. Woodward, with great ingenuity, transforms the above expression into one or other of two rapidly converging series, in either of which he says the first term is sufficient in the case of the earth, if the time since the commencement of the cooling is less than 100,000,000,000 years. The second of these series (no. 20) written in our symbols is

$$u = V - \frac{rV}{r-x} \left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{4\kappa t}}} \epsilon^{-\mu^2} d\mu - \frac{2}{\sqrt{\pi}} \int_{\frac{2r-x}{\sqrt{4\kappa t}}}^{\frac{2r+x}{\sqrt{4\kappa t}}} \epsilon^{-\mu^2} d\mu - \&c. \right\} \dagger$$

The first term of this series being sufficient, if we differentiate it with respect to  $t$  we get

$$\frac{du}{dt} = - \frac{V}{\sqrt{\pi}} \frac{r}{r-x} \frac{x}{t\sqrt{4\kappa t}} \epsilon^{-\frac{x^2}{4\kappa t}}.$$

\* 'Annals of Mathematics,' vol. iii. June 1887.

† The convergency of this series is evidently due to the rapidity with which the definite integral  $\int_0^{\mu} \epsilon^{-\mu^2} d\mu$  approximates to the limiting value  $\frac{1}{2}\sqrt{\pi}$  as the upper limit increases. When that is no greater than 2.17, the first six places of decimals are the same as for the limit, and when it is 4 the first ten.

This differs from the expression for the corresponding time rate ( $dv/dt$ ) in the case when sphericity is neglected by being multiplied by the factor  $r/(r-x)$ . Hence the fall of temperature at a given depth goes on slightly more rapidly in the case of the sphere, as might be expected.

Again, differentiating with respect to  $x$ , we have

$$\frac{du}{dx} = \frac{r}{r-x} V \frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{4\kappa t}} e^{-\frac{x^2}{4\kappa t}} - \frac{r}{(r-x)^2} V \left( 1 - \frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{4\kappa t}} \int_0^{\frac{x}{\sqrt{4\kappa t}}} e^{-\frac{x^2}{4\kappa t}} dx \right).$$

Putting  $x=0$ , we get for the temperature gradient at the surface

$$\beta = V \left( \frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{4\kappa t}} - \frac{1}{r} \right),$$

whence

$$\sqrt{4\kappa t} = \frac{2}{\sqrt{\pi}} \frac{1}{\frac{\beta}{V} + \frac{1}{r}}.$$

When sphericity is neglected, or  $r$  infinite, we have  $\sqrt{4\kappa t} = \frac{2}{\sqrt{\pi}} \frac{V}{\beta}$ , =  $a$  of Lord Kelvin's problem of secular cooling, and as in my 'Physics &c.' Hence the time which elapses before a given surface-temperature gradient is acquired is somewhat shorter when sphericity is taken account of, as might also have been expected.

Lord Kelvin assumed the high value of 7000° F. for  $V$ , the temperature of solidification, probably to allow for its possible increment in the lower shells owing to the pressure. With this value  $a=402,832$  feet. But, when sphericity is taken account of,  $\sqrt{4\kappa t}$  becomes 396,073 feet, which makes it 1 mile and 1497 feet less.

The equation which gives  $x$ , the depth of the level of no strain, is \*—

$$\frac{3e}{(r-x)^2} \int_x^r (r-x)^2 \frac{du}{dt} dx = e(r-x) \frac{du}{dt}.$$

If we substitute the value just found for  $du/dt$ , and take  $\sqrt{4\kappa t}$  for the unit of length, this may be reduced to the

\* 'Physics, &c.,' p. 95.

following equation :—

$$(r-x)(2(r-x)x-3) + 3\epsilon^2 \int_x^r \epsilon^{-x^2} dx = 0.$$

If we make  $x$  zero, the first side of this becomes negative.

If we give  $x$  such a value as will make the first term vanish, it becomes positive. This value is  $\frac{1}{2}(r - \sqrt{r^2 - 6})$ , or to our present unit is 0.028. Hence the value of  $x$  which gives the level of no strain lies between 0 and 0.028, so that  $x^2$  is small, and  $x^3$  and higher powers may be neglected. We may therefore put

$$\begin{aligned} \int_x^r \epsilon^{-x^2} dx &= \int_0^r \epsilon^{-x^2} dx - \int_0^x \epsilon^{-x^2} dx, \\ &= \frac{\sqrt{\pi}}{2} - x, \end{aligned}$$

The equation then becomes

$$(r-x)(2(r-x)x-3) + 3(1+x^2) \left( \frac{\sqrt{\pi}}{2} - x \right) = 0;$$

whence, neglecting  $x^2/r^2$ ,

$$x = \frac{3}{2} \frac{1}{r} - \frac{3\sqrt{\pi}}{4r^2} + \frac{9}{8r^3}.$$

Or, restoring the unit  $\sqrt{4\kappa t}$ ,

$$x = \frac{3}{2} \left( \frac{\sqrt{4\kappa t}}{r} - \frac{\sqrt{\pi}}{2} \frac{(4\kappa t)^{\frac{3}{2}}}{r^2} + \frac{3}{4} \frac{(4\kappa t)^2}{r^3} \right).$$

This differs from the expression when sphericity is not considered, in the small terms. With the values  $1/51^\circ$  F. per foot for the gradient at the surface, and  $7000^\circ$  F. for the temperature of solidification, the depth of the level of no strain was found to be 11,252 feet\*. But the depth when sphericity is taken account of in the cooling will be 11,071 feet; so that the level of no strain is brought *nearer* to the surface by 181 feet by this consideration. The resulting difference, however, comes out so small as amply to justify sphericity being neglected, as was done by Professor Darwin and myself.

It is obvious that the corrugations formed by compression

\* 'Physics &c.,' 2nd edit. p. 98.

will consequently be slightly diminished instead of being increased by the more accurate hypothesis of sphericity.

The present investigation is a sufficient reply to Professor Blake's objection that "English writers have hitherto adopted Lord Kelvin's assumption that the earth may be regarded as of infinite radius, and have thus followed him in using linear equations for the conduction of heat. But when later writers go further, and at the same time introduce the radius of the earth, already assumed infinite, into the calculation, they are obviously inconsistent, and it may well be that the whole of the results are derived from this inconsistency itself." Plausible as this criticism at first sight appears, I have now shown that it is altogether unimportant, seeing that the position of the level of no strain is not appreciably altered when the inconsistency complained of is avoided. At the same time, such alteration as its removal introduces tends in the opposite direction to that which Mr. Blake appears to expect, bringing, as it does, the level of no strain nearer to the surface, and therefore making the resulting elevatory corrugations smaller than before. It may be as well to remind the reader that the depth of the level of no strain in a solid globe does not follow the same law as the radial contraction. The former varies as the time, and therefore the rate at which it descends is constant. The latter varies as the square root of the time, so that the rate at which the surface sinks diminishes as the time increases.

Professor Blake concludes his critique with a formidable list of difficulties to be overcome before "we can really face the problem of a level of no strain." If it is required to find what its situation would be with accuracy, even within a mile or so, no doubt we are not, and probably even our remote descendants will never be, in a position to do so. But this is obscuring the real issue. The reference to "the positive teachings of geological facts" is beside the question. In this connexion these merely tell us that the superficial strata have again and again been ridged up by lateral pressure. But some minds will not rest satisfied with this "positive teaching" without seeking the *cause* of this phenomenon. That it is due to the contraction of the globe through cooling is an hypothesis seemingly simple and by prescriptive right orthodox, but not necessarily true; while the arrangement of the axes of elevation in lines following undeviating directions for immense distances, instead of forming a network of polygons, by no means favours it. But the discovery of a level of no strain affords perhaps the strongest argument against this theory, more especially if the earth is assumed to be solid, as

in the preceding calculations. And it does not seem probable that a better knowledge of the varying conductivity of rocks, or of their contractibility on cooling, would give such altered values to the constants of the problem as to bring up the calculated amount of elevations so as to approach the actual. Dr. Murray estimates the mean elevation of the land of the globe at 1947 feet above the sea, and the mean depth of the ocean at 12,456 feet\*, whereas, according to my estimate, the mean height of the elevations which would be caused by the compression of a solid earth, initially supposed at 7000° F., would be only  $6\frac{1}{2}$  feet†.

If we make the supposition that the crust rests on a liquid substratum, we shall still have a level of no strain‡, and although the amount of the corrugations formed will in this case be somewhat greater, it will still fall far short of that which the "positive teachings of geology" require us to account for.

## XII. *An Improved Form of Littrow Spectroscope.*

By F. L. O. WADSWORTH §.

[Plate VI.]

IT is rather remarkable that in the development of the prismatic spectroscope there have been no important modifications in the general design of the instrument as first used by Newton, progress having been marked mainly in the mechanical improvements of the various parts. Various modifications have, it is true, been proposed from time to time, but none of them has stood the test of usage, except perhaps the form which was first proposed by Littrow in 1862||, and has since been modified and improved by Young and Lockyer¶, Browning\*\*, Grubb††, Bracket‡‡, and others.

In this form, as is well known, the rays from the slit, after being rendered parallel by a collimating-lens, pass through the prism or train of prisms and fall normally upon a plane

\* 'Scottish Geographical Magazine,' June 1888, vol. iv.

† 'Physics, &c.,' 2nd ed. p. 103.

‡ 'Physics, &c.,' Appendix, chap. xxviii.

§ Communicated by the Author.

|| American Journal of Science, 2nd series, vol. xxxv.

¶ Schellen, *Spectralanalyse*, vol. i. p. 231.

\*\* Ibid. p. 237.

†† Monthly Notices of the Royal Astronomical Society, vol. xxxi. p. 36.

‡‡ American Journal of Science, 3rd series, vol. xxiv. p. 60.

reflector, and after reflexion retrace the train in the opposite direction, and are brought to a focus by the same lens which acts as a collimator. To observe conveniently an image of the spectrum, a small right-angled prism covering one half the field is placed near the slit.

In certain respects the advantages of this form over the ordinary one are unquestionably great; for not only does it allow all parts of the instrument, save the prisms and plane reflector, to be fixed in position, but it also involves the use of only one lens, a consideration of some importance in the case of large instruments. Unfortunately in this, its original form, it has two very practical disadvantages:—1st, the general illumination of the field of view by reflexion of a portion of the light from the slit from the surface of the lens; and, 2nd, the close proximity of the observing eyepiece to the slit. Both of these difficulties are avoided in the modified forms already referred to, in which the collimator covers only the lower half of the prism, the plane reflector being replaced by a right-angled prism, which is so placed as to return the ray after two internal reflexions through the upper half of the prism. The observing telescope is consequently entirely above and distinct from the collimator, and can be placed at any angle with the latter (usually it is placed at right angles) by the use of another reflector.

This arrangement, while entirely avoiding both of the difficulties mentioned, introduces others of a different character. In the first place the cost is considerably increased; for two objectives are required, one for the collimator, the other for the observing telescope; the prisms for a given aperture of telescope must be twice as large as before; and, finally, two right-angled prisms both of large size, one having the same aperture as the telescope, the other an aperture about  $1\frac{1}{2}$  times greater, are required. This makes the instrument more expensive even than one of the ordinary form of the same dispersion.

Again, the increase in the number of optical surfaces involved diminishes very considerably both the brightness and the distinctness of the spectral image, and increases the number of adjustments required for accurate spectrometric work.

For all these reasons it is not surprising that these instruments have failed to displace to any extent the standard form; for the only advantage which they possess over that form is their somewhat greater compactness and rigidity, both telescopes being fixed in position. But the simplicity of design and cheapness of construction, which were distinguishing

characteristics of the original Littrow form, have been entirely lost in the attempt to overcome the difficulties already mentioned in regard to the illumination of the field and the inconvenient position of the eyepiece.

More recently Prof. Bracket\* has, without essentially altering the original design of the instrument, overcome the first and principal difficulty, by making the combined collimator and observing lens with faces of such curvature as to reduce the quantity of light reflected to the observing eyepiece to a minimum.

It recently occurred to me, in connexion with an attempt to photograph the spectrum with a spectroscope of this form, that the difficulty could be completely overcome by the use of a concave mirror in place of the lens, and a trial of an instrument so constructed showed that it possessed other advantages also.

The following brief description of this form of instrument, which is, I believe, new, may therefore be of interest. Fig. 2 (Pl. VI.) is a plan view, the top plate of the containing box being removed to show the parts clearly, and fig. 1 is a side view. A small right-angled prism *a* receives the light from the slit *s*, and reflects it to a concave mirror *b* which acts as a collimator. From *b* the collimated beam is reflected to the prism *c*, behind which is the plane mirror *d*, which returns the rays again through the prism to the concave mirror, by which they are finally brought to a focus at the observing eyepiece *f*, which is placed just above the plane of the slit and near the edge of the prism. A blackened screen *L* is placed between the prism and the eyepiece to cut off the light reflected from the faces of the former. A second screen, *L*, is placed between the eye and the slit, or else the beam of light is brought to the latter through a tube or box, as indicated by the dotted lines. Diaphragms *m*, *n* are also placed in front of the eyepiece to cut off any general light diffused from the walls of the enclosing box, which are of course carefully blackened.

It will be readily seen that with this arrangement of apparatus, the only light which can reach the eyepiece besides that which forms the spectral image is that which is diffused by the reflecting surface of the mirror. If this mirror is properly silvered† the general illumination due to this cause will be insignificant, and the field of view will be quite as

\* *Loc. cit.*

† In order to secure a non-diffusive coat of silver, it is necessary to so manage the silvering bath that the deposited film is bright as it comes from the solution and requires no subsequent polishing; for no matter

dark as in the ordinary form of spectroscope. This construction, therefore, overcomes the main objection to the Littrow form, and enables all the advantages of that form to be realized, while it also possesses, as I shall proceed to point out, certain advantages of its own in the way of greater compactness, better definition, and, finally, greater cheapness of construction.

As all parts of the instrument save the concave mirror are close together, they may all be placed on a small base, which even for the largest instrument need not be more than 8 or 10 in. in diameter, as there are no heavy rotating or overhanging parts, as in the other forms of spectroscope.

The concave mirror itself may then be placed on a separate stand and connected with the rest of the apparatus when the instrument is in use, by means of a paper tube or light wooden frame covered with black cloth. Great focal lengths may thus be easily employed without increasing the cost or bulkiness of the instrument, with a corresponding gain in brightness and in definition. Better definition also results from the fact that the number of optical surfaces concerned is less than in any other form of the same dispersive power. Thus in the ordinary Littrow form (one prism) with an achromatic lens there are 8 optical surfaces, and the ray meets 6 of these twice, making 14 reflexions or refractions between the slit and eyepiece. In the ordinary form of equivalent dispersion (two-prism) spectroscope there are 12 surfaces and 12 refractions, while in the concave-mirror form there are only 5 surfaces and 8 refractions or reflexions. Moreover, there is no change of focus for different parts of the spectrum, an advantage of some moment when photographs are being taken, and although the concave mirror is astigmatic when used as here shown, this astigmatism is no disadvantage when viewing the image of a slit, and may

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how great care is taken, minute scratches are sure to be made by the polishing pad.

To obtain such a coat it is necessary:—1st, that great care be taken in cleaning the glass surface; 2nd, that pure chemicals be used for the silvering solution; 3rd, that the temperature of the depositing bath be the same as that of the mirror, and preferably below 70 degrees in order that the deposit may proceed slowly and uniformly. I have obtained good results with both the Rochelle-salts process and the Brashear process; but for this purpose prefer the latter, as it gives a very hard film which may be vigorously rubbed with a pad of absorbent cotton while still wet. The former process, however, is, I think, preferable for “half silvering,” *i. e.* for obtaining a very even semitransparent film.



indeed, in some cases, be a real advantage, as pointed out by Ames in his paper on the concave grating\*. The amount of astigmatism is exceedingly small in an instrument of the dimensions and construction here shown, as the angle between the incident and reflected ray and the geometrical axis is less than one degree.

In the first trial instrument which was constructed after this plan, the focal length of the mirror was about 175 centim. and its aperture a little less than 6 centim. The prism was of white flint of about the same aperture, with a dispersion of  $3\frac{1}{2}$  degrees from A to H. Although the apparatus was mostly made of wood, and the adjustments were in consequence rather rough and unsatisfactory, the results obtained were even better than I had anticipated. The whole spectrum from the extreme violet to the extreme red was very bright and clean, with the lines very sharply defined. With an eyepiece having a magnifying-power of 70 and a slit-width of .01 millim. (at which width the spectrum was almost too bright for comfort), both the Ni line and the lines at 5892 between the D's could be seen, and the doubles in the tail of A were clearly distinguishable†.

The freedom from diffused light may be judged from the fact that the  $\alpha$  and A lines were both clearly seen without the aid of a colour-screen, while with this the lines below A at wave-length 8300 could be seen distinctly without taking any unusual precautions. Better evidence of this point is afforded by photographs of the lower end of the spectrum, which have been taken on an ordinary Cramer Isochromatic plate, whose maximum of sensitiveness lay in the yellowish green. If any considerable amount of diffused light had been present the plates would have been hopelessly fogged by it, as the time of exposure was in some cases nearly an hour. The linear expansion of the spectrum was so small (4.9 centim. from A to D) that some of the detail which was present was masked by reason of the coarseness of the grain of the plate, and a second mirror having a focal length nearly three times as great (470 centim.) was therefore substituted.

\* "Concave Grating in Theory and Practice," *Phil. Mag.* vol. xxvii. p. 369.

† If we define the purity of the spectrum by the relation  $P = \frac{\lambda}{D\phi + \lambda} R$  (*Encyc. Brit. Art. Spectroscopy*), where D is the width of the slit,  $\phi$  the angular value of the collimator aperture, as viewed from the slit, we have, in this case, for yellow light  $P = 0.67 R$ , viz. a purity of nearly 70 per cent. of the theoretical resolving-power of the prism was obtained. With the longer-focus collimator a purity of nearly 80 per cent. was reached.

With this new mirror the advantages of this form of instrument were still more apparent, and the results obtained leave little to be desired. With it photographs of different portions of the spectrum, extending from the violet to the red, have been obtained, which show an amount of sharpness and detail which is, I think, considerably greater than has heretofore been obtained with a single prism of the material and aperture of the one here used.

Two other modifications of the form which have suggested themselves during the course of these experiments are shown in figs. 3 & 4.

In the first of these the collimator is placed in the position occupied by the plane mirror, and the rays pass directly from the slit through the prism without collimation. The slit and spectral image are therefore situated at the two principal conjugate foci of the mirror. In this form, which has been given only a preliminary trial, the definition is, as might have been expected, decidedly inferior to that in the form of the instrument just described. The advantage which this form offers is simply its great simplicity and cheapness, the number of optical surfaces involved being only 4. In the second form (which is not properly a modification of the Littrow form at all, as the rays traverse each prism only once) separate concave mirrors or lenses are used for the collimator and for the view-telescope. The arrangement is shown in fig. 4. A fixed collimating telescope with slit at  $s$  and collimator at  $a$  sends the beam through a prism to a plane mirror  $m$ , by which it is reflected to a second prism  $p$  placed by the side of the first; after passage through which it falls upon the objective of the view-telescope  $T$ , which is also fixed in position, at an angle with the first equal to the angle between the incident and reflected rays on the mirror  $m$ . The prism-table on which the two prisms are mounted is connected with the arm which carries the mirror  $m$  by a minimum-deviation attachment, as in the previous forms. A little consideration will show that the central ray in the field of the  $T$  will always remain at minimum deviation as the arm carrying the mirror  $m$  is revolved. This form has not been actually tried, but would seem to offer certain advantages when it is desirable for any reason to use separate telescopes for collimating and observing.

Astro-Physical Laboratory,  
Smithsonian Institution, Washington, D.C.  
March 1894.

### XIII. Geometrical Interpretation of $\log Uq$ .

By ALEXANDER MACFARLANE.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN the notice of Dr. Molenbroek's *Anwendung der Quaternionen auf der Geometrie*, your reviewer says, "It would probably baffle even a Hamilton to give a geometrical interpretation of  $\log Uq$ " (Phil. Mag. vol. xxxvii. p. 333). As this matter has been treated of in several of my papers, I send you the interpretation required.

The general quaternion  $q$  may be analysed into the product of a ratio and a versor; by  $Uq$  is meant the versor. Let  $\alpha$  denote the axis of the versor and  $A$  its amount in radians, then  $Uq = \alpha^A$  and  $\log Uq = A\alpha'$ ; but  $\log \alpha' = \alpha^{\frac{\pi}{2}}$ , therefore  $\log Uq = A\alpha^{\frac{\pi}{2}}$ . A more correct definition of  $A$  is the ratio of twice the area of the sector to the square of the initial radius; for that definition applies also to a hyperbolic versor.

The geometrical meaning of the above expression will become evident on considering the more general versor given by an equiangular spiral. Let a quinion be denoted by  $q'$ , and let it be defined to be such that

$$\log Uq' = A\alpha^w = A \cos w + A \sin w \cdot \alpha^{\frac{\pi}{2}};$$

we then find that  $A \sin w \cdot \alpha^{\frac{\pi}{2}}$  is the logarithm of the angle and  $A \cos w$  the logarithm of the radius of an equiangular spiral of axis  $\alpha$  and constant angle  $w$ , the initial radius being unity. Thus  $w$  is the constant angle between the radius-vector and the tangent, or rather the difference of the angle from the initial radius to the tangent and that from the initial radius to the radius-vector. In the case of the circle this difference angle is a quadrant: this is the explanation of the quadrantal versor in  $\log Uq$ . In the spiral the quantity  $A$  is the magnitude of the complex logarithm, and  $\alpha^w$  gives the components of the logarithm. The expansion depends on the scalar component of the logarithm, while the rotation depends on the vector component. In the case of the circle, that is of  $Uq$ , the scalar logarithm vanishes.

For further elucidation of this matter consider a hyperbolic quaternion. Let  $p$  denote such a quaternion; when the multiplier is removed we have  $Up = \alpha^{iA}$  and therefore  $\log Up = iA\alpha^{\frac{\pi}{2}}$ .

Here  $A$  is the ratio of twice the area of the hyperbolic sector to the square of the initial radius, and  $\alpha^{\frac{\pi}{2}}$  is the constant sum of the angle from the initial radius to the tangent and that from the initial radius to the radius-vector. This leads us to consider the hyperbolic analogue of the equiangular spiral. Let  $p'$  denote the corresponding hyperbolic quinion; then

$$\log Up' = iA \cdot \alpha^w = iA (\cos w + \sin w \cdot \alpha^{\frac{\pi}{2}}).$$

Here  $w$  denotes the constant sum of the angle between the initial vector and the radius-vector and the angle between the initial vector and the tangent. The scalar term  $iA \cos w$  is the logarithm of the radius-vector, while the vector term  $iA \sin w \cdot \alpha^{\frac{\pi}{2}}$  is the logarithm of the hyperbolic angle. Here  $i$  is the scalar  $\sqrt{-1}$ ; in the papers on "The Principles of Elliptic and Hyperbolic Analysis," and on "The Definitions of the Trigonometric Functions," I have shown that a quantity which is the sum of a scalar independent of  $i$  and another scalar dependent on  $i$  is represented along one straight line.

University of Texas,  
Austin, Texas, U.S.A.,  
May 10, 1894.

ALEXANDER MACFARLANE.

#### XIV. On a Fundamental Question in Electro-Optics.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

**W**ILL you kindly afford me space for a few remarks in connexion with Professor Quincke's letter, which appeared in the May number of this Magazine. The object of that letter was to draw attention to the fact that, in my paper on Electro-Optics which appeared in the April number, I made no mention of a paper of Professor Quincke's, published eleven years ago, which gives an account of experiments by him on the same subject and by similar methods. I think I should preface what I have to say on this matter with an expression of regret for my forgetfulness.

I was well aware of the existence of that paper. I received a copy from the author, and perused it I think immediately on receipt. With regard to the electro-optic effects there described, as given by an interference-refractor, it was evident to me then, as it is now, that they were in their nature and immediate origin essentially different from those pure double refractions that are given regularly by the common polari-

scope and compensator as effects of electrostatic stress. They were evidently produced by mechanical disturbance of the dielectric ; and effects of that kind are of no interest in electro-optics, except as hindrances to exact observation. It may be easily understood, therefore, that I omitted all reference to Professor Quincke's experiments in my paper, not from any positive intention, but because they did not occur to me as contributing in any degree to the solution or illustration of the question that I had in hand.

In this connexion I may notice an old set of experiments of my own upon the same question, which did not occur to me as worth mentioning in my paper, though they had given a clear and striking exhibition of the double refraction. The dielectric was carbon disulphide, the electro-optic field was a very obtuse and very thin prism which extended from end to end of a large plate-cell, and the light (monochromatic and unpolarized) entered and left the cell respectively through the collimator and the telescope of an ordinary spectroscope, the slit being parallel to the lines of force. As the mechanically compressed prisms of glass acted in Fresnel's well-known experiment, so the electrically strained prism of  $\text{CS}_2$  acted here. At high potentials the telescope gave two parallel images of the slit, clearly, though not very widely, separated from each other, and polarized in planes parallel and perpendicular to the lines of force ; but the mechanical disturbance of the dielectric rendered this result useless for my purpose, as it kept the double image of the slit moving incessantly and very irregularly, so that no probable inference could be drawn as to the absolute retardations of the two component rays. I hope to have something more to say about this method and its results hereafter.

There are two statements in Professor Quincke's letter which require some qualification. The first is, that his methods were identical with those followed by myself. This applies truly to the kind of instrumental means employed, and to the general conception of the arrangements, means and methods of great delicacy, for which we are indebted to Professor Jamin, by whom indeed they were put among the common-places of the higher experimental optics. But the method described in my paper includes something more : it deals with the chief difficulty of the subject by detaching the double refraction from the irregular and ever present effects of mechanical disturbance ; and it brings out in this way the fact—clearly enough, perhaps, for a first and imperfect proof—that electric stress acts exclusively on the (Fresnel's) vibration which is directed along the line of force.

The second statement is that Professor Quincke's results were different from mine, that he observed sometimes an increase, sometimes a diminution, of the velocity of light whose plane of polarization is parallel to the lines of force. Our results are not really inconsistent. The phenomena were different because the physical actions examined were different, perhaps as widely different as *conduction* and *convection* in the somewhat similar experimental question of the conduction of heat in fluids.

JOHN KERR.

Glasgow, 18th June, 1894.

## XV. *Notices respecting New Books.*

*Electromagnetic Theory.* By OLIVER HEAVISIDE.  
("The Electrician" Printing and Publishing Company.)

THIS work consists largely of definitions and summaries, and it may be considered as giving something like a bird's-eye view of the more theoretical and recondite portions of electromagnetic science dealt with in Mr. Heaviside's previous, and most valuable, work, 'Electrical Papers.'

Omitting a comparatively short introduction, the present work may be said to contain three long chapters, whose titles are: "Outline of Electromagnetic Connections," "The Elements of Vectorial Algebra and Analysis," and "Theory of Plane Electromagnetic Waves."

Within the limits of an ordinary review it would be impossible to follow Mr. Heaviside in detail in his exposition of the processes at work in the electromagnetic field, even if my knowledge were so complete as to enable me to do justice to every portion of the abstruse and elaborate work for which Mr. Heaviside is so well known. I must therefore confine my remarks to comparatively few of the interesting and important questions so ably dealt with by him; and it will, no doubt, be better if I select chiefly those portions of the work in which he appears *in opposition*, sometimes rightly and sometimes wrongly (according to my judgment) to prevailing views.

A reader of Mr. Heaviside's writings is at once struck by the extraordinary style which distinguishes him from every other English writer on Mathematics or Physics; and the impression which is produced by this style is often the reverse of pleasing. There is a complete absence of the conventionalities which are generally recognized as proper to the writing of a scientific treatise. Mr. Heaviside is the Walt Whitman of English Physics; and, like the so-called "poet," he is certain to raise aversion to his peculiarities. A few typical instances must suffice for quotation. Thus, in p. 142, he pays a well-deserved tribute to printers in the words "Compositors are very intelligent, read mathematics like

winking, and carry out all instructions made by the author." Again (p. 203), when defining the potential produced at any point of space by a vector, he says, "We may use the same definition when it is a vector that has to be potted, or potentialised. Thus, if  $A$  is the potential of  $C$ , then  $A = \text{pot } C = \sum C/4\pi r$ ." Again (p. 352), when discussing the magnetic flux relations, he presents us with the ethical maxim, "Different men have different opinions—some like apples, some like inions"! We can easily imagine the difficulty of some thoroughly zealous and painstaking German translator of this work in his attempt to render this scientific principle into good German. In vain does he consult his English dictionaries for the word "inions"; until, perhaps, after a week's labour, the happy solution occurs to him that "inions" is a misprint for "ions," which are, of course, preferred to apples by those endowed with electrical tastes,—and then the truth of the principle becomes at once obvious.

It was pleasant to find in a previous work that Mr. Heaviside attaches due importance to clearness of expression, and even to grammatical accuracy. In a passage in which he severely criticises the language of a well-known experimentalist, he very truly says "The first step to the understanding of a writer is to find out what he means." Now, if I am not mistaken, this passage affords a key to Mr. Heaviside's peculiar style, and supplies, to a great extent, a justification of it. So far as my own experience of English writers is concerned, it is not a great exaggeration to say that by far the greater portion of my time is occupied in the work of ascertaining the meaning of the author and in overcoming the difficulties of ambiguous language. The *intrinsic* difficulties of the subject demand, in general, a comparatively short time. Thus, the typical English writer in opening up a mathematical discussion on (say) an electromagnetic field, in some portions of which there are wires conveying electrical currents, there being in other portions magnets, dielectrics, conductors, &c., will usually assume the following shroud of vagueness: "Let  $v$  be the velocity,  $C$  the current,  $E$  the electromotive force,  $K$  the specific inductive capacity,  $V$  the potential,  $\mu$  the permeability,  $B$  the induction,  $D$  the displacement,  $H$  the magnetic force,  $L$  the inductance,  $T$  the kinetic energy, &c., &c." After every one of which we exclaim "Of what?" But in vain, the typical author considers that he has bargained to give us the whole bundle of facts and nothing more. In the grave and stilted Scientific Treatise, or Solemn Homily, there must be no touch of imagination to increase the interest of the reader, nor any digression for the purpose of anticipating a misunderstanding, however natural.

It is this characteristic of some of our writers which renders a treatise on the same subject, and with the same scope, by a French author such a welcome relief. In the latter we almost invariably find vagueness, ambiguity, and an illogical order of thought conspicuously absent; and very possibly it is this consideration that has induced Mr. Heaviside to throw over the orthodox style of

writing—though, in so doing, he has occasionally allowed his illustrations and his language to fall into an opposite extreme.

As everyone knows, Mr. Heaviside has advocated many changes in scientific nomenclature, and has already succeeded in getting some of them adopted. The present volume teems with them; but he does not appear (p. 34) to expect success for a very large number.

It is an unfortunate (perhaps an unavoidable) circumstance that, on the appearance of any new branch of science, there is sure to be started a system of nomenclature which, with the advance of knowledge, is soon perceived to be unscientific and misleading. The science of Electricity is far from being an exception to this rule. Its most conspicuous term, Electromotive Force, is thoroughly misleading; and this term Mr. Heaviside replaces, very happily, by the term "Voltage" (p. 26); for, that which is usually called the "electromotive force along any path" is, in reality, the line-integral of the [tangential comp. of the] electric force-intensity from the beginning to the end of that path, and this Mr. Heaviside habitually describes as the Voltage along the path. Analogously, the same integral for the magnetic force-intensity he calls the Gaussage—which, as he takes the trouble to inform us, is "pronounced *Gowsage*, after Gauss (pronounced *Gowce*)"—this latter to replace the absurd "magnetomotive force." Can we imagine the typical English author taking so much trouble to set us right? Mr. Heaviside is usually most scrupulously precise and accurate; but, for a moment, he forgets this characteristic when, at the end of p. 26, he continues:—"The Voltage or the Gaussage along a line is the sum of the effective electric or magnetic forces along the line; the effective component being merely the tangential component of the real" [*i. e.* the resultant] "force." He knows well that the sum of such quantities (infinite in number, and each of finite magnitude) is infinite. The unskilful "practician" should be told that he is not to take the *sum of such components*, but the sum obtained by multiplying each of them by the element of length of the curve, and then adding these products together. And is there not a little slip of the same nature at the top of p. 151 (and elsewhere), where the surface-integral of induction is written  $\sum \mathbf{NBdS}$ ?

With regard to another term in very common use with the practitioners, viz., "lines of force," Mr. Heaviside is justly severe, more particularly in Vol. II. of his 'Papers' (p. 328), where he says "It is quite painful to read of *magnetic resistance to lines of force*." The worst of this matter with regard to lines of force is that a line of force, in the strict Euclidian sense of a line (length without breadth) is a mathematical reality with which the mathematicians cannot dispense, while the *unit tube* of force is also a reality, and quite distinct from the *line*; so that when the practitioner talks of the *number* of lines of magnetic force passing through a given surface, either he employs the notion of tubes while talking of lines, or—and this is, perhaps, what generally happens—he is



talking simple mathematical nonsense, and picturing to himself a charged electric body or a magnetic pole from a fairly large number (!) of points on whose surface emanate *lines*, which may pretty well occupy the space immediately round the body, but which diverge so much from each other at a short distance from it, that space is there practically devoid of lines. The surface of the body, thus conceived, strongly resembles the head of a pepper-caster, while a much more accurate representation would liken it to the surface of a golf ball.

In the same way, another glaring absurdity is visited with just severity (p. 109),—"The utterly vicious misuse of *pressure* to indicate E.M.F. or voltage, by men who are old enough to know better, and do."

Some other terms put forward by Mr. Heaviside do not seem to be so helpful. For example, the ratio of electric displacement to electric force at any point of a dielectric he proposes to call the "permittivity" of the medium, because it indicates "the capacity for *permitting* electric displacement." But a capacity for *permitting* is no more identified with electric displacement than with magnetic; and hence there is nothing definitely suggestive in the word. It can scarcely be doubted that "coefficient of electric elasticity," as applied to its reciprocal, in accordance with usage in the general theory of Elasticity, is a better term—and it is, in fact, explicitly used by Maxwell, vol. i., art. 60; but, unfortunately, Mr. Heaviside expressly rejects this helpful term, which does not tax the memory, on the ground (see 'Papers,' Vol. II. p. 328) that "the prefixing of adjectives is just one of those things that we should try to avoid in a convenient terminology." On the contrary, I think, when the prefixing of an adjective secures clear and proper definition, it should be adopted.

The system of nomenclature is carried somewhat too far. We do not want a name for every coefficient, and a wholly different name for its reciprocal; the list soon becomes too formidable; and it is a little amusing to find Mr. Heaviside, after telling us at p. 21 that  $c$  in the equation  $D=cE$  is the "permittivity" of the medium, telling us at the top of p. 24 that " $c$  is the coefficient of compliance, or the compliancy"—as if he thought that  $c$  still required a little artistic touching. But "compliance" and "compliancy" fail in helpfulness just as much as "permittance" and "permittivity." The truth is that the problem to describe an assigned quality of a body in a single, perfectly definite, and appropriate word no more admits of a solution than does at an arbitrary moment in a game of Chess the corresponding problem to play and mate in one move.

Many people will, perhaps, think that in the word "forcive," for a system of forces, conciseness is again a little overdone.

It must be noted as worthy of commendation that Mr. Heaviside systematically and in explicit terms always identifies the *magnetic induction* at any point in a medium with a flux or displacement, and thereby removes whatever obscurity is contained in Maxwell's

general use of the term, besides bringing the subject more into line with the theory of strain and stress in general. "So far we have considered the two forces, electric and magnetic, producing four fluxes, two involving storage and two waste of energy" (p. 25), the existence of one of these fluxes (namely, the magnetic conduction current) being quite problematical, but nevertheless postulated (as appears farther on) for the purpose of giving formal completeness to the cross connexions of electric and magnetic phenomena, and allowing us to dispense with Maxwell's Vector Potential.

Thus, in Mr. Heaviside's notation, the systematic, concise, and fundamental equations of the electromagnetic field are simply the following:—

$$D=cE, \quad B=\mu H, \quad C=kE, \quad K=gH,$$

$$\rho = \text{div } D, \quad \sigma = \text{div } B,$$

$$C + \dot{D} + \rho q = \text{curl } (H - h_0 - h),$$

$$K + \dot{B} + \sigma q = - \text{curl } (E - e_0 - e),$$

in which  $\rho$  and  $\sigma$  at a point are volume-densities of electrification and "magnetification,"  $q$  is the vector of velocity at the point if the medium is moving,  $K$  is the magnetic conduction current at the point, the other quantities being pretty generally recognizable, while  $K, g, \sigma$  are all of doubtful existence (see more particularly p. 539 of Vol. II. of the 'Papers').

With regard to Mr. Heaviside's notation for vectors—viz., Clarendon type—it may be said that its adoption is impossible for the simple reason that we cannot use it, or anything like it, in our manuscript work; unless, indeed, in addition to pen, ink, and pencil, we keep beside us a camel's-hair brush with a plate of indian ink, and then paint in our vectors when they occur in the work, after the slow manner of the Chinese. Mr. Heaviside is conscious of this difficulty, and he suggests (p. 142) that in manuscript work we should have some distinctive mark for vectors, such as a suffix; so that the vector of electric force-intensity might be written  $E_0$ . There are two objections to this: firstly in the case of such a vector, for example, as that of intrinsic electric force in a medium, for which Mr. Heaviside uses  $e_0$  (in Clarendon type) we should be obliged to write  $e_{00}$  in MS.—which is intolerable, as are also  $B_{10}$  &c.; and secondly it is very undesirable to have our ordinary work (with which we are most concerned, and to which we become most accustomed) written in one language, while our books are written in another; there is a loss of time generated by the unfamiliarity involved in the process. At the same time, Clerk Maxwell's terrible German letters are not to be tolerated for a moment. Perhaps a horizontal bar over the letters is the best, though this is not good.

We are now brought to the consideration of certain other peculiarities of Mr. Heaviside's work. Maxwell was, apparently, the

first to give a distinct title to the vector

$$i\left(\frac{dw}{dy} - \frac{dv}{dz}\right) + j\left(\frac{du}{dz} - \frac{dw}{dx}\right) + k\left(\frac{dv}{dx} - \frac{du}{dy}\right),$$

which is derived from any given vector,  $ui + vj + wk$ . In the first edition of the 'Electricity and Magnetism' he proposed to call the first of these the *version* or *curl* of the second, and subsequently the *rotation*. Mr. Heaviside fixed on the term *curl*, and by this name it is now fairly well known. These two related vectors are of perpetual occurrence in all branches of mathematical physics, and it is well that their relationship should be directly indicated and recognized.

Thus, for example, the condition that a liquid should be capable of being in equilibrium under the action of any assigned force-system ("forceive," as Mr. Heaviside would say) is that at each point in the space occupied by the liquid, the resultant force and its curl should be at right angles to each other. Hence, if we call the primary vector  $\rho$ , Mr. Heaviside always denotes the first-mentioned as "curl  $\rho$ ." The intention is sound and good, but the notation is rather troublesome in the ordinary work of writing, and somewhat tedious in the midst of equations. At the same time, the quaternion notation for the curl  $\rho$ , viz.  $\nabla \nabla \rho$ , seems to interpose in the mind an operation,  $\nabla$ , between  $\rho$  and its curl, and the strength and closeness of the relationship are consequently somewhat impaired. We may, I think, agree with Mr. Heaviside in adopting some simple symbol of direct relationship; and I would suggest that, for ordinary working purposes, the notation

$$\dot{\rho},$$

or something closely resembling it, is an improvement on "curl  $\rho$ ."

Again, the divergence of a vector at any point in space—the amount of the vector, considered as a flux, which, per unit volume, leaves space at the point, as Mr. Heaviside well puts it (Vol. II. of 'Papers,' p. 531)—is simply

$$\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz},$$

or  $-\nabla \nabla \rho$  in quaternions; and this Mr. Heaviside always writes "div  $\rho$ ." For the same reason as before (inconvenience in work) this notation should be improved. Perhaps we may with advantage denote the divergence of  $\rho$  by the notation

$$\rho_{\cdot}$$

Mr. Heaviside devotes a large portion of the present work to two fierce attacks—one on the British Association  $4\pi$  and the other on the Quaternionists.

To begin with the first—it is, of course, well known that if the magnitude of the force exerted between two element-sources (whether small quantities of electricity, or magnetic poles, or

particles of gravitating matter) is taken to be

$$\frac{mm'}{r^2},$$

the normal flux of force-intensity due to any distribution of sources, whether forming a continuous "body" or not, taken at all points outwards through any closed surface in the field, is  $4\pi$  times the total "mass" (or quantity of source) contained within the surface. With the above definition of the force between  $m$  and  $m'$ , this  $4\pi$  will enter into many physical expressions: for example, the force between two electric charges in a dielectric of

"specific inductive capacity"  $K$  is  $\frac{ee'}{Kr^2}$ , and the relation between

displacement and electric force-intensity is  $D = \frac{K}{4\pi} \cdot E$ . This  $4\pi$  seldom fails to excite the wrath of Mr. Heaviside. It is easy to see that its introduction into certain expressions can be avoided by assuming the force between two elements to be

$$k \frac{mm'}{r^2},$$

where, at first,  $k$  is undetermined. With this expression, the normal outward or inward flux of force-intensity through any closed surface will be  $4\pi k$  times the contained "mass;" and if we wish to make this flux of force the exact numerical measure of the contained mass, we must take  $4\pi k = 1$ , i. e.  $k = \frac{1}{4\pi}$ , and then the force between two elements is

$$\frac{mm'}{4\pi r^2},$$

where the  $4\pi$  is no longer irritating to Mr. Heaviside, although the B. A. authorities (quoted by Mr. Heaviside at p. 118) expressly rejected every constant, other than unity, in the expression for the force between two elements as "absurd and useless."

The unit mass, or source, then, in this system is one which acts on an equal one (both supposed homogeneous spheres) with a force of  $4\pi$  dynes when their centres are one centimetre apart; or, again, the unit mass may be defined by saying that it is such that the flux of its force-intensity (i. e. force per same unit) through any closed surface surrounding it is unity. It is, then, on this characteristic of giving a unit flux of force that Mr. Heaviside founds the unit of quantity. But, however desirable it is to get rid of  $4\pi$  in the expressions for a large number of physical constants, it is just as well to point out that from the standpoint of *fundamental principles* a flux of force is not a fundamental entity at all, because it consists of an arithmetical sum of forces which act in all possible directions in space, and therefore it is not of fundamental value—unlike the sum of the *components* of such forces in a single direction. In fact, the conception of such an indiscriminate sum

has resulted in the filling of our text-books on Hydrostatics with almost interminable mathematical problems on that glaring unreality and source of evil, the *whole pressure* of a fluid on a curved surface. Of course a flux of electric force through a closed curved surface in an isotropic dielectric acquires physical reality by means of the fact that the "displacement" through the surface at each point is proportional to the value of the force at the point, and thus the flux of force is a measure of the total displacement through the surface.

This is said, however, without any intention of opposing Mr. Heaviside's proposed definition of a unit mass, or source, but merely for the purpose of showing that something may be said on the other side, and that if the  $4\pi$  is made to disappear from many expressions, it is at the expense of its appearance in others which, under the B. A. system, were free from it. Quite possibly, Mr. Heaviside's system is, on the whole, the simplest and the best.

With regard to his attitude of hostility towards Quaternions—and especially towards Professor Tait's treatise—a little more must be said.

Maxwell is usually said to have made occasional use of *Quaternions* in his great treatise. It is, however, quite true (so far as my general recollection goes) that he merely avails himself of the employment of *vectors*, and that the only conception involved in his vectors is that a vector is a mere *carrier, translator, or directed line of definite length* in space; that, in fact, there is nothing of the *rotation or versor* nature involved in his vectors. Maxwell, then, does not use Quaternions at all; possibly he had no need to do so; he employs simply Vector Analysis—*Orthodox Vector Analysis*, I shall call it, to indicate that it is in harmony with the general principles of Quaternions as enunciated by Hamilton. Now, the signification of a vector has been widened by Hamilton, *without in any way interfering with its vehicular nature*, by endowing it with the power of commanding a rotatory operation. Every unit vector is thus also to be looked upon as optionally standing for the operation of quadrantal rotation in planes perpendicular to the direction of the vector, *if we desire so to employ it*. Mr. Heaviside never desires to employ it in this way; he finds it unnecessary to do so in Electromagnetism. Hence he will have nothing whatever to do with the versor property in the vector. "Once a vector, always a vector" (p. 301). His vector is like the heir to a title, or to a large property, who repudiates his hereditary advantage and insists on adopting poverty. Probably he would say that it is rather to be likened to a man born with an ugly tumour who insists on having it cut off. But "different men have different opinions, &c." according to his own previously quoted maxim.

Now, in the Hamiltonian system, if  $i$  is any unit vector,  $i^2 = -1$ ; if  $\alpha$  is any vector of length  $a$ ,  $\alpha^2 = -a^2$ ; and if  $\alpha$  and  $\beta$  are any two vectors of lengths  $a$ ,  $b$ , including an angle  $\theta$ ,  $S\alpha\beta = -ab \cos \theta$ . The minus sign in these results is gall and wormwood to the anti-quaternionists. Of course there is nothing at all strange in

the equation  $i^2 = -1$  if we read it " $i$  repeated equals  $-1$ ," i. e., equals complete reversal; if we read it " $i$  squared  $= -1$ ," our early algebraic feelings are shocked—Mr. Heaviside is amazed at it (p. 303)!

Hence with the anti-quaternionist  $S\alpha\beta = +ab \cos \theta$ . Again, with Hamilton the vector of the product  $\alpha\beta$ , i. e.  $V\alpha\beta$ , follows at once naturally as a vector perpendicular to the plane of  $\alpha$  and  $\beta$ , of length  $ab \sin \theta$ , because  $\alpha\beta = \frac{\alpha}{\beta^{-1}}$ , which is the operation of converting  $\beta^{-1}$  into  $\alpha$ . Now this is done by rotation round the perpendicular to their plane; and as a vector stands for rotation—so that  $\epsilon^m$  signifies rotation through  $m$  right angles round the line coinciding with the unit vector  $\epsilon$ —it is clear that  $V\alpha\beta$  is perpendicular to both  $\alpha$  and  $\beta$ , and in a definite sense. With the anti-quaternionists  $V\alpha\beta$  does not follow naturally at all; it is perfectly arbitrary—provided, of course, that there is something at once definite and consistent in its representation. It might, for example, be very well defined as being of length  $\frac{a}{b} \tan \theta$ , and as

lying in the plane of the bisector of  $\theta$  and the perpendicular to the plane of  $\alpha$  and  $\beta$ , and inclined at (say)  $\theta$  to this perpendicular. However, the anti-quaternionists agree to make  $V\alpha\beta$  exactly what Hamilton made it, and we need not stop to inquire whether any adequate reasons for this can be found from their point of view.

Hence, then, results Mr. Heaviside's system of Vector Analysis, which we may call *Heretical Vector Analysis*, without necessarily implying any censure, since what is orthodox is sometimes false and bad, and what is heretical true and good.

It is not very easy to discover whether Mr. Heaviside's opposition to Quaternions is *absolute* or not; that is, whether he thinks that the subject is one which may be studied as a branch of pure mathematics by advanced speculators, but postponed to the study of Vector Analysis. If, on the one hand, he thinks that the Hamiltonian system (involving the versor property of vectors, &c.) is not worthy of study, the quaternionists might, perhaps, show what the system has achieved or is capable of achieving; but even this is not incumbent on them, for they may justify the study simply for its value as a mental exercise—as other branches of pure mathematics are accepted. The problem of disentangling the quaternion  $q$  from the equation  $q^2 + aq + b = 0$ , where  $a$  and  $b$  are given quaternions, is a perfectly legitimate exercise of thought, even though it has no application to telephony or to dynamo machines. The utility of associating the versor property with vectors is illustrated in a striking way in a fundamental case by Hamilton ('Elements of Quaternions,' p. 370) thus:—If  $\alpha, \beta, \gamma$  are the vectors from the centre of a sphere of unit radius to any three points, A, B, C, on its surface, and if, in addition, these last denote the magnitudes of the angles of the spherical triangle, we have (with the versor meanings attached to  $\alpha, \beta, \gamma$ ) the equation

$$\gamma^{\frac{2C}{\pi}} \beta^{\frac{2B}{\pi}} \alpha^{\frac{2A}{\pi}} = -1,$$

or what is perhaps more obvious,

$$\gamma^{\frac{2(\pi-C)}{\pi}} \beta^{\frac{2(\pi-B)}{\pi}} \alpha^{\frac{2(\pi-A)}{\pi}} = +1;$$

from which we have at once

$$\gamma^{\frac{2(\pi-C)}{\pi}} \beta^{\frac{2(\pi-B)}{\pi}} = \alpha^{\frac{-2(\pi-A)}{\pi}},$$

which, as Hamilton observes, contains at a glance the whole doctrine of spherical triangles. But if, on the other hand, we are to understand that the study of Quaternions is to be merely postponed, then Heretical Vector Analysis will not serve as an introduction. No system which makes  $i^2 = +1$  and  $S\alpha\beta = +ab \cos \theta$  can possibly serve as a preliminary to Quaternions; and as there is nothing intrinsically base in the sign *minus*, or in the notation for a scalar, the reason for replacing Orthodox by Heretical Vector Analysis disappears.

Among the changes of quaternionic notation made by Mr. Heaviside we may further notice that he proposes (p. 157) to denote the tensor of the vector of  $\alpha\beta$ , *i. e.*  $TV\alpha\beta$ , by the symbol  $V_\alpha\beta$ , which surely is quite inappropriate and incapable of adoption.

Again, he says (p. 135) "no amount of familiarity will make Quaternions an easy subject." True—and necessarily true, moreover, when we consider the wideness of the field of thought in which Quaternions work. But neither is it all child's play in Heretical Vector Analysis. The expression  $\alpha\beta$  is no more the same as  $\beta\alpha$  in this department than in Quaternions, and the same careful picking of steps is necessary in both.

Most students of Professor Tait's treatise on Quaternions will, I think, be satisfied that Mr. Heaviside's criticisms on this work are not well founded. "After muddling my way somehow through the lamentable quaternionic Chapter II., the third chapter was tolerably easy" (p. 174). Farther on (p. 289) the objection becomes more definite: "There is the fundamental Chapter II. wherein the rules for the multiplication of vectors are made to depend upon the difficult mathematics of spherical conics, combined with versors, quaternions, and metaphysics." This language is surely a little loose and unjust. One article in Tait's Chapter II., marked with a star to indicate its postponement, and therefore unessential character for the reader, proves the simple property of spherical conics involved. Moreover, to be accurate, it is not the multiplication of vectors that is dealt with here, but the multiplication, &c., of quaternions in general. There is a good deal of difficult mathematics associated with spherical conics, as any reader of Salmon's 'Geometry of Three Dimensions' will see; but not one particle of it is involved in this short Article of Tait's

book : the sum total of the mathematics employed is contained in the text of the two propositions of the third book of Euclid which assert that if any line drawn through a point  $O$  meet a circle in  $P$  and  $Q$ , the rectangle  $OP \cdot OQ$  is constant, and that the sum of a pair of opposite angles in a quadrilateral inscribable in a circle is two right angles.

Mr. Heaviside concludes his third chapter with a discussion of a linear operator in general (p. 283), and the means of inverting it, together with a deduction of Hamilton's cubic. The linear operator is treated all through by Mr. Heaviside exactly as it appears in the general theory of strain and stress—namely, as consisting of coefficients expressing the relations between the three components of one vector and those of another, these coefficients being, in general, nine, as when the components of strain in a solid are expressed in terms of direction ; but sometimes reducing to six, as when components of stress are expressed in terms of direction.

Mr. Heaviside's mode of treatment will be found to be a valuable side-light to the discussion of the linear vector function in Tait's treatise. Of course, the rather high-sounding phrase "inversion of a linear operator" denotes nothing more than the solution of three homely simple equations ; nevertheless, there are some neat relations involved.

This review has already gone much beyond the usual limits, and, in confining itself chiefly to controversial matters, has omitted to notice the most valuable portion of Mr. Heaviside's work, the greater part of which appears in the last chapter. This part of the work has recently been treated, with great commendation, by Professor Fitzgerald in 'The Electrician.' All readers of this volume will agree in regarding it as an able work, and, indeed, one which is of immense assistance to advanced students in Physics.

One final instance of Mr. Heaviside's regard for accuracy and desire for scientific completeness must be mentioned. It is found in Art. 192, in which he justly objects to the equation by which Maxwell expresses the relation between magnetic induction, magnetic force, and magnetization at any point of a medium, viz.,  $B = H + 4\pi I$ . To this Mr. Heaviside objects that it makes induction and magnetization identical in kind with magnetic force, which, as he says, "is more than mischievous in theory." His own form of the equation,  $B = \mu_0(1 + k)F$ , where  $F$  is the magnetic force, is in all respects much better.

G. M. MINCHIN.



## XVI. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from vol. xxxvii. p. 419.]

January 10th, 1894.—W. H. Hudleston, Esq., M.A., F.R.S.,  
President, in the Chair.

**T**HE following communications were read :—

1. 'On the Rhætic and some Liassic Ostracoda of Britain.' By  
Prof. T. Rupert Jones, F.R.S., F.G.S.

2. 'Leigh Creek Jurassic Coal-Measures of South Australia: their  
Origin, Composition, Physical and Chemical Characters; and Recent  
Subaerial Metamorphism of Local Superficial Drift.' By James  
Parkinson, Esq., F.G.S., F.C.S.

This paper contains an account of the lignitic coal of Leigh  
Creek and associated rocks. Analyses are given, as illustrating  
comparisons between the Leigh Creek coal and Jurassic and other  
coal-bearing rocks found elsewhere. The Author discusses the  
origin of the Leigh Creek deposits, and describes certain peculiarities  
noticeable in the superficial materials, which he discusses in another  
paper.

3. 'Physical and Chemical Geology of the Interior of Australia:  
Recent Subaerial Metamorphism of Eolian Sand at ordinary  
atmospheric temperature into Quartz, Quartzite, and other Stones.'  
By James Parkinson, Esq., F.G.S., F.C.S.

South of the Flinders Range fragments of stone of all sizes are  
found on the ground, the origin of which the Author discusses. He  
maintains that they were formed by subaerial metamorphism of  
Eolian deposits.

January 24th.—W. H. Hudleston, Esq., M.A., F.R.S.,  
President, in the Chair.

The following communications were read :—

1. 'The Ossiferous Fissures in the Valley of the Shode, near  
Ightham, Kent.' By W. J. Lewis Abbott, Esq., F.G.S.

2. 'The Vertebrate Fauna collected by Mr. Lewis Abbott from  
the Fissure near Ightham, Kent.' By E. T. Newton, Esq., F.R.S.,  
F.G.S.

XVII. *Intelligence and Miscellaneous Articles.*

ON THE DEPENDENCE OF THE PHOTOELECTRIC CURRENT ON THE POSITION OF THE PLANE OF POLARIZATION OF THE EXCITING LIGHT IN REFERENCE TO THE SURFACE OF THE KATHODE.  
BY DR. J. ELSTER AND H. GEITEL.

**I**T is possible in many cases to lower the potential required for the spontaneous discharge of an electric current in a gas by exposing the kathode to the action of light. For the same difference of potential the strength of the current depends on the nature of the kathode, the gas, and the light. While kathodes of platinum, mercury, copper, and several other metals require irradiation with ultra-violet light of high intensity, kathodes of sodium, potassium, rubidium, in an atmosphere of hydrogen of about 0·3 millim. pressure, give currents which can be measured galvanometrically, even with feeble light within the region of the visible rays.

The question may be asked whether this action of light on the electrical discharge depends on the orientation of the vibrations with respect to the surface of the electrode struck.

Experiments with polarized ultra-violet light of sufficient intensity are difficult to make because it is absorbed by the ordinary polarizing arrangements, such as Nicol's prism, tourmaline plates, glass disks, &c., so that only polarization by reflexion remains; even with this method, however, great losses of light are unavoidable. Thus in an analogous phenomenon, the development of electrical sparks by ultra-violet light discovered by Hertz, M. Wanka did not succeed in establishing the influence of the direction of vibration of the light, which he had supposed to exist.

This difficulty disappears with kathodes of the alkaline metals, since we can here work with ordinary polarized light; but another difficulty presents itself, that a polished and, if possible, a plane surface of these substances must be produced in a vacuum. This requirement is, however, satisfied by using as kathode the alloy of potassium and sodium, which is liquid at ordinary temperatures. When placed in a roomy receiver a sufficient quantity sets plane and horizontal in the central part of the surface.

We have investigated the photoelectric action of polarized light as follows.

In the circuit of a voltaic battery of about 250 volts are a sensitive galvanometer, a commutator, and a sensitive cell of the liquid potassium and sodium alloy of the form shown in Wiedemann's *Annalen*, vol. xlii. p. 564, so inserted that the negative-pole wire leads to the surface of the alkali metal. In order that the active luminous pencil should have a constant section, the cell was coated with opaque varnish, with the exception of a small circle of 15 millim. diameter turned towards the source of light. The cell is so arranged that the rays entering this aperture centrally and parallel strike the centre of the metal surface under an angle of about 65°. Between the source of light and the cell a lens was introduced for the production of parallel light as well as a polarizing arrangement (a Nicol's prism or a set of glass plates).

If the polarizing apparatus is turned while at the same time the strength of the current is measured at the galvanometer, two maxima and two minima are observed in the course of a single rotation. The minima occur when the plane of polarization of the light is parallel to the plane of incidence of the rays on the kathode; the maxima are in positions at an angle of  $90^\circ$  with them. The ratio of maxima to minima is about 10 : 1. If while the plane of polarization is parallel to the plane of incidence, a quartz plate about 2 millim. thick, cut at right angles to the optical axis, is placed in the path of the polarized light, the current increases about sevenfold, corresponding with the rotation of the plane of polarization due to the quartz. When the plane of polarization is at right angles to the plane of incidence, a quartz plate has the opposite effect; the strength of the current diminishes, as was to be expected, in a corresponding ratio. Apart from a slight enfeeblement of the current due to the loss of light caused by its interposition, a clear glass plate has no effect in either position.

According to the investigations of MM. Trouton ('Nature,' vol. xxxix. p. 393), Klemencić (Wiedemann's *Annalen*, vol. xlv. p. 77), and Righi (*Rend. della R. Acc. dei Lincei*, vol. xi. p. 161) it must be taken for granted that, in Hertz's rays of electrical force, the plane of polarization is at right angles to the direction of the electrical displacement. If the motion in the light rays is regarded as analogous, the result of the experiments described would be thus expressed.

The luminous electrical current attains its maximum when the electrical displacements in the luminous ray take place in the plane of incidence, its minimum when they are at right angles thereto. In the former case the electrical vibrations contain a component normal to the kathode, but not in the second. We might be tempted to seek in these changes of potential normal to the kathode, and induced by the electrical rays, the force which impels the negative electricity to leave the kathode. Whether this suggestion is correct, can perhaps be ascertained by further experiments on the dependence of the luminous electrical action on the angle of incidence of the polarized light, and their connexion with the quantities of light reflected from and retained by the kathode.—*Berliner Berichte*, February 8, 1894. (*Communicated by the Authors.*)

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ON VORTEX MOTIONS IN AIR. BY G. QUINCKE.

At the meeting of the Natural History and Medical Society of Feb. 7, 1890, I discussed the motion of falling spheroids of oil in water, the specific gravity of which was increased somewhat by the addition of chloroform. Such a spheroid falls vertically in water at rest. But if two spheroids of oil fall simultaneously close to each other, they approach and recede from each other in falling. The path and the time of fall depend on the distance apart and the velocity of the falling spheroids. This peculiar motion is caused by the vortices which are produced by the falling spheroids of oil in the water about them, which had hitherto

been at rest. The particles of water in the plane of symmetry between the falling spheroids remain at rest.

Instead of two spheres, one may be allowed to fall near a plane vertical wall, which then acts as plane of symmetry. The spheroid falls as it were with its image in the plane vertical wall, and approaches and recedes from this.

These experiments with heavy oil spheroids in water are tedious, and can only be shown to a small audience.

Analogous phenomena may be produced before a larger circle of hearers by allowing two soap bubbles filled with coal-gas to ascend near each other, or a single bubble near a vertical wall.

In ascending, the distance of the two soap bubbles from each other, or of a single one from its image in the vertical wall, is first smaller and then greater, and the cause again is the vortex movements in the air due to the ascending soap bubbles.

In order to fill two soap bubbles simultaneously with coal-gas they are produced at the ends of a T-piece of glass, blown out in the form of horizontal cups, to which the gas passes from the centre tube through a T-shaped perforated glass stopper.

Similar phenomena occur when small dust particles fall in air or liquid at rest, or if a current of air or liquid strikes against particles of dust at rest. The motion of the small particles is influenced by the presence and form of the solid wall in the vicinity.—Wiedemann's *Annalen*, July 1894.

#### ON A NEW APPARATUS FOR THE PRODUCTION OF HIGH PRESSURE.

BY PROF. S. W. STRATTON\*.

Not long since, while designing a piece of apparatus for the production of high pressure, it occurred to me that many of the difficulties encountered in the measurement of such pressures might be avoided by the employment of several short mercury-columns connected in series by means of a less dense liquid, as shown in the accompanying sketch.

Such a gauge would possess all the advantages of the ordinary mercury-column, and be within the limits of space to be had in the laboratory. For many purposes the last tube only need be made of glass, and the scale reduced accordingly.

Thinking that this principle may be new, and of value to some who are employing high pressures in the laboratory, it is submitted for publication.

The Ryerson Physical Laboratory,  
University of Chicago,  
May 21, 1894.

\* Communicated by Prof. A. A. Michelson.



THE  
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AND  
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

AUGUST 1894.

XVIII. *An Examination into the Physical Consequences of the Local Alteration of the Material of Isotropic Spheres or Spherical Shells under Uniform Surface-Pressure.* By C. CHREE, M.A.\*

*Simple Shell; Strains and Stresses.*

§ 1. **T**HE equilibrium of an isotropic sphere or spherical shell under uniform surface-pressure is one of the oldest problems satisfactorily treated in elastic solids. It is necessary, however, to consider it briefly here, as preliminary to the main object of this paper, which treats from a physical standpoint of a sphere or a spherical shell composed of several concentric layers of different isotropic materials. This latter problem is not altogether new mathematically †, but the points to which attention is principally directed here have not, I believe, been previously considered.

The displacement  $u$  is at every point along the radius vector  $r$  from the centre. The principal strains are

$$\frac{du}{dr} \equiv s \text{ along the radius,}$$

and two equal strains

$$u/r \equiv s'$$

\* Communicated by the Author.

† See 'Quarterly Journal of Pure and Applied Mathematics,' vol. xxi. p. 193 (1886).



The quantity  $S$  is termed the *stress difference*, and its greatest value, viz.

$$\bar{S} = \frac{3}{2} (p' \sim p) \frac{a^3}{a^3 - e^3}, \quad . \quad . \quad . \quad . \quad (10)$$

occurring at the inner surface, is called the *maximum stress difference*.

Here it is assumed that

$$3k > 2n. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If this relation failed to hold, a bar of the material would increase in radius when exposed to longitudinal traction, and I am not aware that such a striking phenomenon has yet been observed in an isotropic material.

The signs, whether positive or negative, of the strains, the dilatation, and the stresses for *pressure* over one only of the two surfaces are given in Table I.

TABLE I.

		$s$		$s'$ .	$\Delta$ .	$(-\widehat{rr})$ .	$\widehat{\theta\theta}$ .
		when $\frac{r}{e} < \left(\frac{3k}{2n}\right)^{\frac{1}{3}}$	when $\frac{r}{e} > \left(\frac{3k}{2n}\right)^{\frac{1}{3}}$				
$p$ alone acting }	—	—	+	+	+	+	
$p'$ alone acting }	+	—	—	—	+	—	

We shall employ the notation  $\delta s$  &c. to denote increments in  $s$  &c. answering to increments of any size  $\delta p$  or  $\delta p'$  in  $p$  and  $p'$ . The expressions for  $s$  &c. being linear in  $p$  and  $p'$ , the above table shows at once the signs of  $\delta s/\delta p$  &c. when one only of the surface-pressures is altered.

The two most important quantities are probably  $\Delta$  and  $(-rr)$ . The value of  $\Delta$  is constant, the volume expanding uniformly under pressure at the inner surface, and contracting uniformly under pressure at the outer surface. The radial stress is always a pressure.

If  $p' = 0$ , then

$$\frac{p - (-rr)}{p} = \frac{r^3 - e^3}{r^3} \frac{a^3}{a^3 - e^3};$$

while if  $p = 0$ ,

$$\frac{p' - (-rr)}{p'} = \frac{a^3 - r^3}{r^3} \frac{e^3}{a^3 - e^3}.$$

Thus, in both cases, as we recede from the surface where

the pressure is applied, the falling off in the radial pressure over a concentric spherical surface varies directly as the volume between the surface considered and that where the pressure is applied, and inversely as the volume within the surface considered. Of two equal volumes of the material, that nearer the centre is the more effective in reducing the radial pressure.

*Linear Relation between three Stresses or three Strains.*

§ 3. It is hardly necessary to point out that if (*e. a. a.*), instead of being a simple shell, were a layer of a compound shell, the results (4)–(10) would still apply to it, if *p* and *p'* were taken equal to the pressures exerted on its inner and outer surfaces respectively by the material of the adjacent layers.

Suppose, now, that in a simple shell, or in a single layer of a compound shell, we take any three concentric spherical surfaces of radii  $r_1, r_2, r_3$ . Let us denote the volumes they contain, viz.  $\frac{4}{3}\pi r_1^3$  &c., by  $V_1, V_2, V_3$ , and the radial pressures over their surfaces by  $p_1, p_2, p_3$  respectively. By means of (7) we easily find a linear relation between the three pressures. This may be written in various equivalent forms, of which the most elegant is perhaps

$$p_1\left(\frac{1}{V_2} - \frac{1}{V_3}\right) + p_2\left(\frac{1}{V_3} - \frac{1}{V_1}\right) + p_3\left(\frac{1}{V_1} - \frac{1}{V_2}\right) = 0. \quad (12)$$

Relations of exactly the same form hold between the values of  $\widehat{\theta\theta}$ , or those of any the same strain, over the three surfaces.

If  $s_1, s_2, s_3$ , for instance, be the values of *s*, or  $\frac{du}{dr}$ , over the three surfaces we have

$$s_1\left(\frac{1}{V_2} - \frac{1}{V_3}\right) + s_2\left(\frac{1}{V_3} - \frac{1}{V_1}\right) + s_3\left(\frac{1}{V_1} - \frac{1}{V_2}\right) = 0. \quad (13)$$

If, then, we know the values of any strain or stress at any two radial distances in a simple shell, we have at once its value at any other radial distance. The above results (12) and (13) apply equally to a solid sphere or to any single layer of a compound shell. They bear a distant family resemblance to the well-known “theorem of the three moments”\* in beams, usually associated with the name of Clapeyron.

\* See Todhunter and Pearson’s ‘History of Elasticity,’ vol. ii. art. 603; or Love’s ‘Treatise on Elasticity,’ vol. ii. art. 221.



### Three-layer Compound Shell.

§ 4. We now proceed to consider the effects arising from the application of the pressures  $p$  and  $p'$  over the inner and outer surfaces of the three-layer compound shell ( $e . \alpha . c . \alpha_1 . b . \alpha . a$ ). In this a layer ( $c . \alpha_1 . b$ ) of material  $k_1, n_1$  is intercalated between the layers ( $e . \alpha . c$ ) and ( $b . \alpha . a$ ) both composed of material  $k, n$ .

The strains and stresses that would exist if the shell were all of the material  $k, n$  are given by (4)–(8). Our principal object is to find the additions made to the strains and stresses in ( $e . \alpha . c$ ) and ( $b . \alpha . a$ ) in consequence of the existence of the layer ( $c . \alpha_1 . b$ ), which we shall generally denote the “altered layer.” To do this we have only to find the increments  $\delta p_b$  and  $\delta p_c$  to the pressures  $p_b, p_c$  at the surfaces  $r=b$  and  $r=c$  of the altered layer. The changes in the strain and stress in ( $b . \alpha . a$ ) arise solely from the action of the pressure  $\delta p_b$  over  $r=b$ , while the changes in the strain and stress in ( $e . \alpha . c$ ) arise solely from the action of the pressure  $\delta p_c$  over  $r=c$ . When  $\delta p_b$  and  $\delta p_c$  are known, the corresponding strains and stresses may be written down at once from (4)–(8).

The values of  $\delta p_b$  and  $\delta p_c$  are easily found as follows:—The shell ( $b . \alpha . a$ ) is in equilibrium under the pressures  $p_b + \delta p_b$  and  $p'$  over its inner and outer surfaces, while the shell ( $c . \alpha_1 . b$ ) is in equilibrium under the pressures  $p_c + \delta p_c$  and  $p_b + \delta p_b$  over its inner and outer surfaces. We thus know by (5) the values of the strain  $s'$  in the two layers in terms of these pressures. But  $s' = u/r$ , and  $u$  is necessarily continuous at the common surface  $r=b$  of the two media; thus we have  $s'$  continuous, whence

$$\frac{1}{a^3 - b^3} \left\{ (p_b + \delta p_b) b^3 \left( \frac{1}{3k} + \frac{1}{4n} \frac{a^3}{b^3} \right) - p' a^3 \left( \frac{1}{3k} + \frac{1}{4n} \right) \right\} = \frac{1}{b^3 - c^3} \left\{ (p_c + \delta p_c) c^3 \left( \frac{1}{3k_1} + \frac{1}{4n_1} \right) - (p_b + \delta p_b) b^3 \left( \frac{1}{3k_1} + \frac{1}{4n_1} \frac{c^3}{b^3} \right) \right\}. \quad (14)$$

Similarly from the continuity of  $s'$  at  $r=c$  we find

$$\frac{1}{c^3 - e^3} \left\{ p e^3 \left( \frac{1}{3k} + \frac{1}{4n} \right) - (p_c + \delta p_c) c^3 \left( \frac{1}{3k} + \frac{1}{4n} \frac{e^3}{c^3} \right) \right\} = \frac{1}{b^3 - c^3} \left\{ (p_c + \delta p_c) c^3 \left( \frac{1}{3k_1} + \frac{1}{4n_1} \frac{b^3}{c^3} \right) - (p_b + \delta p_b) b^3 \left( \frac{1}{3k_1} + \frac{1}{4n_1} \right) \right\}. \quad (15)$$

These two equations determine  $p_b + \delta p_b$  and  $p_c + \delta p_c$  in terms

of  $p$  and  $p'$ , while  $p_b$  and  $p_c$  are obtained at once by writing  $b$  for  $r$  and  $c$  for  $r$  respectively in (7).

Carrying out the necessary reductions we find

$$\delta p_b = \frac{(b^3 - c^3)(a^3 - b^3)}{\Pi(bc)^3(a^3 - e^3)} \left[ 3k(n_1 - n) \{ k_1(3k + 4n)e^3 + 4n(k_1 - k)(c^3 - e^3) \} \frac{p' - p}{b^3} \right. \\ \left. + 4n(k_1 - k) \{ n_1(3k + 4n)c^3 - 3k(n_1 - n)(c^3 - e^3) \} \frac{p'a^3 - pe^3}{(ea)^3} \right], \quad (1)$$

$$\delta p_c = \frac{(b^3 - c^3)(c^3 - e^3)}{\Pi(bc)^3(a^3 - e^3)} \left[ 3k(n_1 - n) \{ k_1(3k + 4n)a^3 - 4n(k_1 - k)(a^3 - b^3) \} \frac{p - p'}{c^3} \right. \\ \left. + 4n(k_1 - k) \{ n_1(3k + 4n)b^3 + 3k(n_1 - n)(a^3 - b^3) \} \frac{pe^3 - p'a^3}{(ea)^3} \right], \quad (2)$$

where, for shortness,

$$\Pi \equiv \frac{a^3 - e^3}{(ea)^3} kn(3k + 4n)(3k_1 + 4n_1) \\ + (b^3 - c^3) \left[ (3k + 4n) \left\{ \frac{3kk_1(n_1 - n)}{(bc)^3} + \frac{4nn_1(k_1 - k)}{(ea)^3} \right\} \right. \\ \left. + 12kn(k_1 - k)(n_1 - n) \frac{(c^3 - e^3)(a^3 - b^3)}{(abce)^3} \right]. \quad (18)$$

The quantity  $\Pi$  is essentially positive.

To facilitate reference it will be well to record explicitly the changes in the strains, dilatation, stresses, and stress-difference in the two layers. In (*b.a.a*) we have

$$\delta s \equiv \left( \frac{du}{dr} \right) = -\delta p_b \frac{b^3}{a^3 - b^3} \left( -\frac{1}{3k} + \frac{1}{2n} \frac{a^3}{r^3} \right), \quad (19)$$

$$\delta s' \equiv \frac{\delta u}{r} = \delta p_b \frac{b^3}{a^3 - b^3} \left( \frac{1}{3k} + \frac{1}{4n} \frac{a^3}{r^3} \right), \quad (20)$$

$$\delta \Delta = \delta p_b \frac{b^3}{a^3 - b^3} \cdot \frac{1}{k}, \quad (21)$$

$$\delta(\widehat{rr}) = \delta p_b \frac{b^3}{a^3 - b^3} \left( \frac{a^3}{r^3} - 1 \right), \quad (22)$$

$$\delta(\widehat{\theta\theta}) = \delta p_b \frac{b^3}{a^3 - b^3} \left( 1 + \frac{1}{2} \frac{a^3}{r^3} \right), \quad (23)$$

$$\delta S = \pm \delta p_b \frac{b^3}{a^3 - b^3} \cdot \frac{3}{2} \frac{a^3}{r^3}. \quad (24)$$

The existence of the common factor  $\delta p_b \frac{b^3}{a^3 - b^3}$  will be noticed.

In (*e. α. c*) we have

$$\delta s = -\delta p_c \frac{c^3}{c^3 - e^3} \left( \frac{1}{3k} - \frac{1}{2n} \frac{e^3}{r^3} \right), \quad . \quad . \quad . \quad (25)$$

$$\delta s' = -\delta p_c \frac{c^3}{c^3 - e^3} \left( \frac{1}{3k} + \frac{1}{4n} \frac{e^3}{r^3} \right), \quad . \quad . \quad . \quad (26)$$

$$\delta \Delta = -\delta p_c \frac{c^3}{c^3 - e^3} \frac{1}{k}, \quad . \quad . \quad . \quad . \quad . \quad (27)$$

$$\delta(-\widehat{rr}) = \delta p_c \frac{c^3}{c^3 - e^3} \left( 1 - \frac{e^3}{r^3} \right), \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$\delta \widehat{\theta\theta} = -\delta p_c \frac{c^3}{c^3 - e^3} \left( 1 + \frac{1}{2} \frac{e^3}{r^3} \right), \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$\delta S = \pm \delta p_c \frac{c^3}{c^3 - e^3} \frac{3}{2} \frac{e^3}{r^3}. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

The existence of the common factor  $\delta p_c \frac{c^3}{c^3 - e^3}$  will be noticed.

We shall consider the phenomena relating to the pressures  $p$  and  $p'$  separately. By reference to Table I. we know the signs of the strains and stresses in the simple shell (*e. α. a*), and when the signs of  $\delta p_b$  and  $\delta p_c$  are determined from (16) and (17) we know the signs of the increments to the strains and stresses in (*b. α. a*) and (*e. α. c*).

§ 5. If first pressure be applied over the inner surface only, or  $p'$  be zero, the signs of  $\delta p_b$  and  $\delta p_c$  are shown in the following Table II. for the cases most likely to arise in practice.

TABLE II.

$p$  only existing.

$\begin{cases} n_1 - n \\ k_1 - k \end{cases}$	+	+	0	—	0	—
$\delta p_b$	—	—	—	+	+	+
(except when $e/c$ and $b/a$ both very small.)						
$\delta p_c$	+	+	+	—	—	—

The columns of signs are to be taken each separately. The first column, for instance, gives the signs of  $\delta p_b$  and  $\delta p_c$  when  $n_1 - n$  and  $k_1 - k$  are both positive. It seems hardly practicable to lay down concise general rules for what happens when  $n_1 - n$  and  $k_1 - k$  have opposite signs, but the results in any specified case may be derived of course from (16) and (17).

If next pressure be applied over the outer surface only, or  $p$  be zero, we obtain the results embodied in Table III.

TABLE III.

$p'$  only existing.

$\begin{cases} n_1 - n \\ k_1 - k \end{cases}$	$\begin{matrix} + \\ + \end{matrix}$	$\begin{matrix} + \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ + \end{matrix}$	$\begin{matrix} - \\ 0 \end{matrix}$	$\begin{matrix} - \\ - \end{matrix}$	
$\delta p_b$	$+$	$+$	$+$	$-$	$-$	$-$
$\delta p_c$	$-$	$-$	$-$	$+$	$+$	$+$ (except when $e/c$ and $b/a$ both very small).

From Tables II. and III. we see that if  $n_1 - n$  and  $k_1 - k$  be both positive, or if one be positive and the other zero,  $\delta p_b$  is negative and  $\delta p_c$  positive when  $p$  only exists; whereas  $\delta p_b$  is positive and  $\delta p_c$  negative when  $p'$  only exists. This signifies that if pressure be applied at either surface of a shell the intercalation of a layer of greater  $k, n$  raises the radial pressure at the surface of the layer nearest to the surface where the pressure is applied, and lowers it at the other. In other words, as we retire from the surface of the shell where the pressure is applied the radial pressure falls more slowly—*i. e.* has a less steep *gradient*—throughout the material on both sides of the layer of greater  $k, n$  than previous to the alteration of the layer, and makes up for this by an accelerated rate of falling throughout the layer itself.

The phenomena when one of the two  $n_1 - n$  and  $k_1 - k$  is negative and the other zero are exactly opposite to the above, and the same is also in general true when  $n_1 - n$  and  $k_1 - k$  are both negative; but in the latter event an exception may arise when  $e/c$  and  $b/a$  are both very small, especially when the altered layer differs considerably from the remainder.

### *Effects on Dilatation.*

§ 6. The effect on the dilatation due to the existence of the altered layer claims special attention. When  $n_1 - n$  and  $k_1 - k$  are both positive, or one positive and the other zero, we see, by reference to equations (21) and (27), and to Tables II. and III., that  $\delta\Delta$  is negative in both (*b. a. a*) and (*e. a. c*) when  $p$  only exists, and is positive in both when  $p'$  only exists. Thus it follows by (6) that  $\delta\Delta$  is opposite in sign to  $\Delta$  in both (*b. a. a*) and (*e. a. c*). In other words, the presence of the layer of greater  $k, n$  reduces numerically\* the dilatation—

\* To avoid complexity the statement in the text is limited to suit the general case where the changes  $\delta\Delta$  are not large enough to cause a reversal of sign in the dilatation. Such a reversal occurs, however, in one

whether expansion following internal pressure  $p$ , or contraction following external pressure  $p'$ —throughout the unaltered material both outside and inside of it.

The exact opposite holds if  $n_1 - n$  and  $k_1 - k$  be one negative the other zero, or if both be negative, a possible exception arising in the latter case when  $e/c$  and  $b/a$  are both very small.

Whilst the changes of the dilatation in  $(b . \alpha . a)$  and  $(e . \alpha . c)$  due to the existence of the altered layer agree in general qualitatively, they usually differ quantitatively.

For if  $\Delta_0 + \delta\Delta$  refer to  $(e . \alpha . c)$  and  $(\Delta_0 + \delta\Delta_2)$  to  $(b . \alpha . a)$ —the dilatation in the simple shell  $(e . \alpha . a)$  under the same pressures being  $\Delta_0$ —we easily find

$$\delta\Delta_2 - \delta\Delta = 3 \frac{b^3 - c^3}{(bc)^3} \frac{n_1 - n}{\Pi} \left[ p \left\{ k_1(3k + 4n) - 4n(k_1 - k) \frac{a^3 - b^3}{a^3} \right\} - p' \left\{ k_1(3k + 4n) + 4n(k_1 - k) \frac{c^3 - e^3}{e^3} \right\} \right]. \quad (31)$$

Thus in general there is a difference between the dilatations in  $(b . \alpha . a)$  and  $(e . \alpha . c)$  which increases with the volume of the altered layer, and is more conspicuous the closer this layer to the inner surface of the compound shell.

If  $n_1 = n$ ,

then  $\delta\Delta_2 = \delta\Delta$ .

Thus if the altered layer retain the same rigidity as the rest the dilatations in  $(b . \alpha . a)$  and  $(e . \alpha . c)$  remain equal, however much the altered layer may differ from the rest in compressibility.

The coefficient of  $p$  in (31) is easily shown to be essentially positive, and that of  $p'$  is obviously so. Thus when  $n_1 - n$  is positive, and  $k_1 - k$  is positive or zero,  $\delta\Delta_2 - \delta\Delta$  has the same sign as  $p$  when  $p'$  is zero, and the opposite sign to  $p'$  when  $p$  is zero.

Now when  $p$  only exists  $\Delta_0$  is positive, and  $\delta\Delta_2$  and  $\delta\Delta$  are both negative when  $n_1 - n$  is positive and  $k_1 - k$  is positive or zero. It follows that under these circumstances the presence of the altered layer is more effective in reducing the dilatation in  $(e . \alpha . c)$  than in reducing that of  $(b . \alpha . a)$ .

exceptional case when  $p$  only exists, viz. when the intercalated layer is of exceptionally large rigidity and lies close to the inner surface of the shell, while  $a/b$  is large. The expansion naturally accompanying pressure on the inner surface may then be converted into an absolute contraction throughout the thin inner layer  $(e . \alpha . c)$ .

Again, when  $p'$  only exists  $\Delta_0$  is negative, and  $\delta\Delta_2$  and  $\delta\Delta$  are positive when  $n_1-n$  is positive and  $k_1-k$  is positive or zero; thus the presence of the altered layer reduces the contraction in  $(e.\alpha.c)$  more than that in  $(b.\alpha.a)$ .

Thus, whether there be pressure on the outer surface alone or the inner surface alone, the presence of the layer  $(b.\alpha_1.c)$ , in which the rigidity exceeds and the bulk modulus equals or exceeds that of the remainder, has a greater effect on the density of the contained layer  $(e.\alpha.c)$  than on that of the surrounding layer  $(b.\alpha.a)$ .

It is equally easy to show that the density of  $(e.\alpha.c)$  is in general more affected by the existence of the altered layer than is that of  $(b.\alpha.a)$  when  $n_1-n$  is negative, with a possible exception in the case of pressure on the outer surface when  $k_1-k$  is also negative and  $e/c$  is very small.

§ 7. The general effect of the existence of the altered layer is, as we have seen, to diminish or to increase the effects of surface-pressure in changing the density of the unaltered material according as the elastic constants of the altered layer are greater or less than those of the unaltered material.

The converse question naturally presents itself, viz., how the change of density of the altered layer compares with that in the simple shell  $(e.\alpha_1.a)$ , all of the same material as the layer, exposed to the surface-pressures  $p$  and  $p'$ .

If we regard the dilatation as  $\Delta_1$  in  $(e.\alpha_1.a)$ , and as  $\Delta_1+\delta\Delta_1$  in  $(c.\alpha_1.b)$  when there is the compound shell  $(e.\alpha.c.\alpha_1.b.\alpha.a)$ , we easily find from what precedes \* that

$$\begin{aligned} & \Pi\delta\Delta_1 k_1 (a^3 - e^3) = \\ & p \left[ 4nn_1(k_1 - k)(3k + 4n) \frac{a^3 - b^3 + c^3 - e^3}{a^3} \right. \\ & \quad + \frac{3k(n_1 - n)}{(bc)^3} \left\{ k_1(3k + 4n)(a^3 c^3 - b^3 e^3) \right. \\ & \quad \left. \left. - 4n(k_1 - k) \frac{(a^3 - b^3)(b^3 - c^3)(c^3 - e^3)}{a^3} \right\} \right] \\ & - p' \left[ 3kk_1(n_1 - n)(3k + 4n) \frac{a^3 c^3 - b^3 e^3}{(bc)^3} \right. \\ & \quad + \frac{4n(k_1 - k)}{e^3} \left\{ n_1(3k + 4n)(a^3 - b^3 + c^3 - e^3) \right. \\ & \quad \left. \left. - 3k(n_1 - n) \frac{(a^3 - b^3)(b^3 - c^3)(c^3 - e^3)}{(bc)^3} \right\} \right]. \dots (32) \end{aligned}$$

\* Since neither  $k$  nor  $n$  appears in (7) the radial pressures over  $r=b$  and  $r=c$  are the same in  $(e.\alpha_1.a)$  as in  $(e.\alpha.a)$  so that  $\delta\Delta_1$  equals the dilatation in a simple shell  $(c.\alpha_1.b)$  due to surface-pressures  $\delta p_b$  and  $\delta p_c$  as given by (16) and (17).

The coefficients of  $k_1 - k$  and of  $n_1 - n$  inside the square brackets in the coefficients of both  $p$  and  $p'$  may be shown to be essentially positive.

Having regard to the signs of  $\Delta_1$  in the several cases we at once obtain the result that when  $n_1 - n$  and  $k_1 - k$  are both positive, or one positive and the other zero, the layer (*c. a. b*) suffers more alteration of density in consequence of the application of  $p$  or  $p'$  than if the whole shell were of material  $k_1, n_1$ . In other words, when the layer has larger elastic constants than the remainder it suffers more alteration in its density than if the entire shell consisted of the same material as the layer.

### *Alteration of material small.*

§ 8. The preceding results apply irrespective of the magnitudes of  $(k_1 - k)/k$  and  $(n_1 - n)/n$ , provided these be neither infinitely great nor infinitely small, and so hold however great be the differences of the two materials.

The case when the material is nominally the same throughout, but the elastic constants vary slightly with  $r$ , seems not unlikely to be of frequent occurrence in practice. The law of variation of the elastic constants in such a case is probably in general a continuous function of  $r$ , still the variation may not infrequently be practically restricted to a thin layer. It thus seems worth while glancing briefly at the special case when  $(n_1 - n)/n$  and  $(k_1 - k)/k$  are so small that terms containing their squares or product may be neglected. In this case, putting for shortness

$$\left. \begin{aligned} 3k/(3k+4n) &= N, \\ 4n/(3k+4n) &= K, \end{aligned} \right\} \dots \dots \dots (33)$$

we get from (16) and (17)

$$\frac{(a^3 - b^3)(b^3 - c^3)}{(a^3 - e^3)^2} \left\{ \frac{n_1 - n}{n} N \left( \frac{e^2 a}{b^2 c} \right)^3 (p' - p) + \frac{k_1 - k}{k} K \frac{p' a^3 - p e^3}{b^3} \right\}, \quad (34)$$

$$\frac{(b^3 - c^3)(c^3 - e^3)}{(a^3 - e^3)^2} \left\{ \frac{n_1 - n}{n} N \left( \frac{e a^2}{b c^2} \right)^3 (p - p') + \frac{k_1 - k}{k} K \frac{p e^3 - p' a^3}{c^3} \right\}. \quad (35)$$

If

$$n_1 = n,$$

or the altered layer differ from the rest only in compressibility, we have

$$\frac{b^3}{a^3 - b^3} \delta p_b = \frac{-c^3}{c^3 - e^3} \delta p_c = \frac{b^3 - c^3}{a^3 - e^3} \frac{k_1 - k}{k} K \frac{p' a^3 - p e^3}{a^3 - e^3} \dots \dots \dots (36)$$

Referring to equations (19) to (24) and (25) to (30) we see this implies that the influence of the altered layer on the strains and stresses of the remainder depends only on the volume and not at all on the position of the layer.

In the coefficient of  $(k_1 - k)/k$  in both (34) and (35)  $p'$  occurs multiplied by  $a^3$  and  $p$  occurs multiplied by  $e^3$ . Thus a layer differing slightly from the rest only in compressibility has a greater effect on the strains and stresses arising from a pressure over the outer surface than on those arising from a pressure over the inner surface of the compound shell.

If in (34) and (35)

$$k_1 = k,$$

we have

$$\left( \frac{b^3}{a^3 - b^3} \delta p_b \right) \frac{1}{e^3} = \left( \frac{-c^3}{c^3 - e^3} \delta p_c \right) \frac{1}{a^3} = \frac{b^3 - c^3}{(a^3 - e^3)^2} \frac{n_1 - n}{n} N \left( \frac{ea}{bc} \right)^3 (p' - p). \quad (3)$$

Referring to equations (19) to (24) and (25) to (30) we see that the effect of the layer of altered rigidity, when its volume is given, is greater the nearer it is to the centre.

The layer in this case, however, is as effective in modifying the strains and stresses arising from internal pressure as those arising from external pressure.

#### *Displacements in general case of 3 Layers.*

§ 9. When  $(n_1 - n)/n$  and  $(k_1 - k)/k$  are not small it will be sometimes more convenient, especially when the volume of the altered layer is considerable, to deal with the complete values of the displacements, strains, and stresses than with the increments to the values in the simple shell (*e. a. a.*). The strains and stresses may easily be written down from the displacements, so it will suffice to give the complete values of the latter. These are as follows,  $\Pi$  being given as before by (18):—

In (*e. a. c.*)

$$\begin{aligned} u = \frac{1}{\Pi} \left[ \frac{1}{3} r \left\{ \frac{pe^3 - p'a^3}{(ae)^3} n(3k + 4n)(3k_1 + 4n_1) \right. \right. \\ \left. \left. - 3p \frac{b^3 - c^3}{(abc)^3} (n_1 - n)(k_1(3k + 4n)a^3 - 4n(k_1 - k)(a^3 - b^3)) \right\} \right. \\ \left. + \frac{1}{4r^2} \left\{ (p - p')k(3k + 4n)(3k_1 + 4n_1) \right. \right. \\ \left. \left. + 4p \frac{b^3 - c^3}{(ab)^3} (k_1 - k)(n_1(3k + 4n)b^3 + 3k(n_1 - n)(a^3 - b^3)) \right\} \right]. \quad (3) \end{aligned}$$



In  $(c . \alpha_1 . b)$

$$u = \frac{3k+4n}{\Pi} \left[ \frac{1}{3} r \left\{ \frac{p}{(ab)^3} (n_1(3k+4n)b^3 + 3k(n_1-n)(a^3-b^3)) \right. \right. \\ \left. \left. - \frac{p'}{(ce)^3} (n_1(3k+4n)c^3 - 3k(n_1-n)(c^3-e^3)) \right\} \right. \\ \left. + \frac{1}{4r^2} \left\{ \frac{p}{a^3} (k_1(3k+4n)a^3 - 4n(k_1-k)(a^3-b^3)) \right. \right. \\ \left. \left. - \frac{p'}{e^3} (k_1(3k+4n)e^3 + 4n(k_1-k)(c^3-e^3)) \right\} \right]. \quad (39)$$

In  $(b . \alpha . a)$

$$u = \frac{1}{\Pi} \left[ \frac{1}{3} r \left\{ \frac{pe^3-p'a^3}{(ae)^3} n(3k+4n)(3k_1+4n_1) \right. \right. \\ \left. \left. - 3p' \frac{b^3-c^3}{(bce)^3} (n_1-n)(k_1(3k+4n)e^3 + 4n(k_1-k)(c^3-e^3)) \right\} \right. \\ \left. + \frac{1}{4r^2} \left\{ (p-p')k(3k+4n)(3k_1+4n_1) \right. \right. \\ \left. \left. + 4p' \frac{b^3-c^3}{(ce)^3} (k_1-k)(n_1(3k+4n)c^3 - 3k(n_1-n)(c^3-e^3)) \right\} \right]. \quad (40)$$

These expressions may seem a little heavy, but it should be remembered that in any specified individual case the somewhat lengthy constant coefficients are replaced by concise numerical quantities.

### Two-layer Shell.

§ 10. All the formulæ established for the three-layer compound shell  $(e . \alpha . c . \alpha_1 . b . \alpha . a)$  may easily be modified so as to apply to the simpler case of a two-layer compound shell. Supposing this to be  $(e . \alpha_1 . b . \alpha . a)$  we put  $c=e$  in the previous formulæ, while if it were  $(e . \alpha . c . \alpha_1 . a)$  we should put  $b=a$ .

Taking for example  $(e . \alpha_1 . b . \alpha . a)$ , and regarding  $(e . \alpha_1 . b)$  as the altered layer, we have by (17)

$$\delta p_e = 0,$$

and by (16)

$$\delta p_b = \frac{(b^3-e^3)(a^3-b^3)}{\Pi(b^3)(a^3-e^3)} (3k+4n) \left[ 3kk_1(n_1-n) \left( \frac{e}{b} \right)^3 (p'-p) \right. \\ \left. + 4nn_1(k_1-k) \frac{p'a^3-pe^3}{a^3} \right], \quad (41)$$

where

$$\Pi = (3k + 4n) \left[ \frac{a^3 - e^3}{(ae)^3} kn(3k_1 + 4n_1) + \frac{b^3 - e^3}{e^3} \left\{ \frac{3kk_1(n_1 - n)}{b^3} + \frac{4nn_1(k_1 - k)}{a^3} \right\} \right] \dots (42)$$

Substituting from (41) for  $\delta p_b$  in equations (19) to (24), we get the increments which, added to the corresponding results (4) to (9), give the complete values of the displacements &c. throughout the unaltered material (*b.a.a*). The increments themselves measure, of course, the effects of an alteration of the material at the inner surface from *k, n* to *k<sub>1</sub>, n<sub>1</sub>*. The value of  $\delta p_e$  and the corresponding increments (25) to (30) obtained for (*e.a.c.a<sub>1</sub>.a*), as explained above, would give the effects of a similar alteration at the outer surface.

A comparison of these results will be found to emphasize the fact that a change of rigidity is much more effective at the inner than at the outer surface of a thick shell.

### *Solid Sphere.*

§ 11. The results for a solid sphere under uniform surface-pressure may easily be derived from those for a shell.

In a simple sphere (*0.a.a*), under surface-pressure *p'*, the displacement is deduced from (5) by taking *e* zero, and the strains and stresses are thence easily written down. We thus get:—

$$s' \equiv u/r = -\frac{1}{3} \frac{p'}{k} = s, \dots (43)$$

$$\Delta = -p'/k, \dots (44)$$

$$\widehat{rr} = \widehat{\theta\theta} = -p', \dots (45)$$

$$S = 0. \dots (46)$$

These results may also be derived from the corresponding strains and stresses in the shell (*e.a.a*), by omitting all terms multiplied by *e*, even though a power of *r* occurs in the denominator. Perhaps an even simpler method of reduction consists in supposing *p* = *p'*.

For the compound sphere (*0.a.c.a<sub>1</sub>.b.a.a*) we may, as in the case of the compound shell, proceed in either of two ways. We may start with the results for the simple sphere (*0.a.a*) and find the increments in the displacements, strains, &c., depending on the increments  $\delta p_b$  and  $\delta p_e$  of pressure at

the surfaces of the altered layer ; or we may take the complete values of the displacements. In either case we arrive at much simpler results than for the compound shell.

For the increments of pressure we find in place of (16) and (17),

$$p_b = 4p' \frac{(b^3 - c^3)(a^3 - b^3)}{\Pi'(ab)^3} (k_1 - k)n(3k + 4n_1), \quad . \quad . \quad . \quad (47)$$

$$p_c = -4p' \frac{b^3 - c^3}{\Pi'(ab)^3} (k_1 - k) \{n_1(3k + 4n)b^3 + 3k(n_1 - n)(a^3 - b^3)\}, \quad (48)$$

where

$$\begin{aligned} \Pi' = k(3k + 4n)(3k_1 + 4n_1) + 4 \frac{b^3 - c^3}{(ab)^3} (k_1 - k) \{n_1(3k + 4n)b^3 \\ + 3k(n_1 - n)(a^3 - b^3)\}. \quad . \quad . \quad (49) \end{aligned}$$

If

$$k_1 = k,$$

then, however  $n_1$  and  $n$  may differ,

$$\delta p_b = \delta p_c = 0,$$

whence

$$u = -\frac{1}{3}rp'/k$$

throughout the whole of the unaltered material.

For the displacements in the compound sphere we find in place of (38), (39), and (40),  $\Pi'$  being given by (49), in (0.  $\alpha$ .  $c$ )

$$u = -\frac{1}{3} \frac{rp'}{\Pi'} (3k + 4n)(3k_1 + 4n_1); \quad . \quad . \quad . \quad (50)$$

in ( $c$ .  $\alpha_1$ .  $b$ )

$$u = -\frac{p'}{\Pi'} (3k + 4n) \left[ \frac{1}{3}r(3k + 4n_1) + \frac{c^3}{r^2}(k_1 - k) \right]; \quad (51)$$

in ( $b$ .  $\alpha$ .  $a$ )

$$\begin{aligned} u = -\frac{p'}{\Pi'} \left[ \frac{1}{3}r \{ (3k + 4n)(3k_1 + 4n_1) + 12 \frac{b^3 - c^3}{b^3} (n_1 - n)(k_1 - k) \} \right. \\ \left. - \frac{1}{r^2} (b^3 - c^3)(k_1 - k)(3k + 4n_1) \right]. \quad (52) \end{aligned}$$

One of the most noticeable phenomena in a simple sphere is the vanishing\* of the stress-difference  $S$  at every point.

\* See Phil. Mag. September 1891, pp. 240-42.

The value of  $S$  in the compound sphere is thus of special interest. For it we easily find :—

in  $(0 . \alpha . c)$ ,

$$S = 0 ;$$

in  $(c . \alpha_1 . b)$ ,

$$S = 6p' \left( \frac{c}{r} \right)^3 \frac{(k_1 \sim k)n(3k + 4n)}{\Pi'} ; \quad \dots \quad (53)$$

in  $(b . \alpha . a)$ ,

$$S = 6p' \frac{b^3 - c^3}{r^3} \frac{(k_1 \sim k)n(3k + 4n_1)}{\Pi'} . \quad \dots \quad (54)$$

Since  $S$  varies as  $b^3 - c^3$  in  $(b . \alpha . a)$ , it follows that the stress-difference will there remain small so long as the altered layer is of small volume until  $p'$  becomes very large.

In  $(c . \alpha_1 . b)$ , however,  $S$  depends on the volume of the altered layer only in so far as that enters into  $\Pi'$ , and is thus of importance, however thin the layer may be, provided it differ considerably from the rest in compressibility.

It is hardly necessary to point out the loophole this affords to supporters of the stress-difference theory\* of rupture, if experiment should seem to decide against them.

#### *Any number of Layers.*

§ 12. The compound shell formed of any number of concentric layers of different materials may be treated in the same way as the three-layer shell ; but probably it is quite as easy to express the displacement in each layer in terms of arbitrary constants and determine these from the continuity of the radial displacement and stress.

Let there be  $i$  layers, the radii of the  $(i+1)$  surfaces reckoned from within outwards being  $a_0, a_1, \dots a_i$ . The  $s$ th layer is thus that the radii of whose bounding surfaces are  $a_{s-1}$  and  $a_s$ . The volume of the  $s$ th layer, *i. e.*  $4\pi(a_s^3 - a_{s-1}^3)/3$ , is denoted by  $v_s$ , and its elastic constants by  $k_s$  and  $n_s$ . The notation

$$\left. \begin{aligned} 4n_s/(3k_s + 4n_s) &= K_s, \\ 3k_s/(3k_s + 4n_s) &= N_s = \left( \frac{a_{s-1}a_s}{a_0a_i} \right)^3 M_s \end{aligned} \right\} \quad \dots \quad (55)$$

is also used.

I shall merely record the value of the displacement in the  $s$ th layer in some special forms of the general case, the pressures  $p$  and  $p'$  being applied as before over the inner and outer surfaces respectively of the compound shell :—

\* See Phil. Mag. September 1891, pp. 240-2.

Subcase (i).  $k$  varying, but  $n$  same throughout :—

$$u = r \frac{pa_0^3 - p'a_i^3}{(3k_s + 4n)(a_i^3 - a_0^3)} \left\{ 1 - \sum_1 (K_q v_q/v) \right\}^{-1} \\ + \frac{1}{4r^2} \frac{(a_0 a_i)^3}{n(a_i^3 - a_0^3)} \left[ p - p' - \frac{pa_0^3 - p'a_i^3}{(a_0 a_i)^3} \times \right. \\ \left. \frac{a_s^3 K_s - a_i^3 \sum_1^s (K_q v_q/v) - a_0^3 \sum_{s+1}^i (K_q v_q/v)}{1 - \sum_1^i (K_q v_q/v)} \right]. \quad (56)$$

Subcase (ii).  $n$  varying, but  $k$  same throughout :—

$$u = \frac{1}{3} \frac{r}{k(a_i^3 - a_0^3)} \left[ pa_0^3 - p'a_i^3 \right. \\ \left. - (p - p') \frac{a_{s-1}^3 M_s - a_0^3 \sum_1^s (M_q v_q/v) - a_i^3 \sum_{s+1}^i (M_q v_q/v)}{1 - \sum_1^i (M_q v_q/v)} \right] \\ + \frac{1}{r^2} \frac{(a_0 a_i)^3 (p - p')}{(3k + 4n_s)(a_i^3 - a_0^3)} \left\{ 1 - \sum_1^i (M_q v_q/v) \right\}^{-1} \dots \dots (57)$$

Subcase (iii). Elastic constants departing from mean values  $n$  and  $k$  by small quantities, *e. g.*  $\delta n_s$  and  $\delta k_s$  in the *sth* layer, whose squares and products are negligible:—

$$u = \frac{1}{3} \frac{r}{k(a_i^3 - a_0^3)} \left[ (pa_0^3 - p'a_i^3) \left\{ 1 - N \frac{\delta k_s}{k} - K \sum_1^i \left( \frac{v_q}{v} \frac{\delta k_q}{k} \right) \right\} \right. \\ \left. - (p - p') (a_0 a_i)^3 N \left\{ a_0^3 \sum_1^s \left( \frac{v_q}{v} \left( \frac{1}{a_{q-1} a_q} \right)^3 \frac{\delta n_q}{n} \right) \right. \right. \right. \\ \left. \left. + a_i^3 \sum_{s+1}^i \left( \frac{v_q}{v} \left( \frac{1}{a_{q-1} a_q} \right)^3 \frac{\delta n_q}{n} \right) - a_s^{-3} \frac{\delta n_s}{n} \right\} \right] \\ + \frac{1}{4r^2} \frac{(a_0 a_i)^3}{n(a_i^3 - a_0^3)} \left[ (p - p') \left\{ 1 - K \frac{\delta n_s}{n} - N (a_0 a_i)^3 \sum_1^i \left( \frac{v_q}{v} \left( \frac{1}{a_{q-1} a_q} \right)^3 \frac{\delta n_q}{n} \right) \right\} \right. \\ \left. - \frac{pa_0^3 - p'a_i^3}{(a_0 a_i)^3} K \left\{ a_i^3 \sum_1^s \left( \frac{v_q}{v} \frac{\delta k_q}{k} \right) + a_0^3 \sum_{s+1}^i \left( \frac{v_q}{v} \frac{\delta k_q}{k} \right) - a_s^3 \frac{\delta k_s}{k} \right\} \right]. \quad (58)$$



leaves the total volume of each material unchanged, and does not disturb the material next the surface considered.

Noticing the value of  $M_q$  in (55), we see from (57) that a given alteration of rigidity throughout a given volume has a greater effect the nearer the altered volume to the centre. We have already come across this phenomenon in § 8.

In the compound solid sphere the case when the layers, though differing in rigidity, have all the same compressibility is singularly simple, the same formula (60) supplying the displacement throughout the different layers.

*Directions of no Extension.*

§ 13. In a simple solid sphere exposed to uniform surface-pressure every unit element alters in length to the same extent irrespective of its direction or position in the sphere. In a simple shell ( $e . \alpha . a$ ) it is otherwise : there is in general at any point a conical surface separating directions along which elements lengthen from those along which they shorten. This cone has the diameter through the point considered for axis, and its semi-vertical angle  $\theta$  is given by the equation

$$\cos^2 \theta = \frac{s'}{s' - s} = \frac{1}{3} + \frac{4n}{9k} \left( \frac{r}{ae} \right)^3 \frac{pe^3 - p'a^3}{p - p'}. \quad (62)$$

If  $p' = 0$  this becomes

$$\cos^2 \theta = \frac{1}{3} + \frac{4n}{9k} \left( \frac{r}{a} \right)^3, \quad \dots \quad (63)$$

and, assuming as before

$$3k > 2n,$$

this gives a possible value for  $\theta$  for all values of  $r$ . The directions along which elements shorten are included within the conical surface.

If  $p = 0$  then (62) becomes

$$\cos^2 \theta = \frac{1}{3} + \frac{4n}{9k} \left( \frac{r}{e} \right)^3, \quad \dots \quad (64)$$

which supplies a possible value for  $\theta$  only when

$$r/e < (3k/2n)^{\frac{1}{3}}.$$

By means of the stress-strain relations the equation determining  $\theta$  may easily be thrown into the form

$$\cos^2 \theta = \frac{u}{r} \left( k + \frac{4}{3} n \right) \div \left\{ 3k \frac{u}{r} - \widehat{rr} \right\}, \quad \dots \quad (65)$$

provided  $\widehat{rr} - 3ku/r$  be not zero\*. This applies at any point of a simple shell or of a layer of material  $k, n$  in a compound shell.

We may write the above in the form

$$3k - \left(k + \frac{4}{3}n\right) \sec^2 \theta = \widehat{rr} \div (u/r).$$

Now  $\widehat{rr}$  and  $u/r$  are continuous at a common surface of two contiguous layers of a compound shell. Thus, distinguishing corresponding quantities in two such layers by dashed and undashed letters respectively, we find at the common surface

$$(3k + 4n) \sec^2 \theta - (3k' + 4n') \sec^2 \theta' = 9(k - k'). \quad (66)$$

This relation connecting  $\theta$  and  $\theta'$  depends solely on the material of the layers, and not at all on the radius of their common surface. It should, however, be noticed that if a layer of material  $k', n'$  were intercalated between two layers of material  $k, n$ , the values of  $\cos \theta'$  at its two surfaces would differ, so that  $\theta$  has different values at the inner surface of the outer layer of material  $k, n$  and at the outer surface of the inner layer of the same material.

#### *Linear Relation between Changes of Volume.*

§ 14. In conclusion, I would call attention to a simple and concise relation between the changes of volume or the dilations of the layers composing a compound shell or solid sphere exposed to uniform pressure.

If  $k$  be the bulk modulus of a volume  $v$  of an isotropic material exposed to surface-forces whose components at the point  $x, y, z$  on the element  $dS$  of surface are  $F, G, H$  per unit of surface, then the increment of the total volume,  $\delta v$ , due to the action of these forces, is given by

$$3k\delta v = \iint (Fx + Gy + Hz) dS, \quad \dots \quad (67) \dagger$$

the integral being taken over the entire surface.

Suppose now we apply this to the several layers of which a compound shell is composed. The surface-integrals taken for any two contiguous layers over their common surface clearly vanish. Thus, summing the equations like (67) for the several layers, nothing remains on the right-hand side but the integrals referring to the inner and outer surfaces of the

\* It is zero in the core of a compound sphere, and in every layer of a compound shell of uniform compressibility.

† See Trans. Camb. Phil. Soc. vol. xv., equation (23) p. 318.



shell. Supposing these to be of radii  $e$  and  $a$ , the applied pressures being  $p$  and  $p'$ , we thus find

$$\Sigma(k \cdot \delta v) = \frac{4}{3} \pi (pe^3 - p'a^3). \quad (68)$$

Since the dilatation of a layer is uniform throughout, it is given by

$$\Delta = \delta v/v.$$

We may thus write (68) in the alternative form

$$\Sigma(k \cdot \Delta \cdot v) = \frac{4}{3} \pi (pe^3 - p'a^3). \quad (69)$$

For a solid sphere we have

$$\Sigma(k \cdot \delta v) = \Sigma(k \cdot \Delta \cdot v) = -\frac{4}{3} \pi a^3 p'. \quad (70)$$

The relation we have established is of course insufficient by itself to determine the dilatation in any one layer of a compound shell or sphere, but it at least supplies a very simple check on the accuracy of results otherwise determined. For the three-layer shell ( $e \cdot a \cdot c \cdot a_1 \cdot b \cdot a \cdot a$ ) it gives, denoting the dilatations in ( $e \cdot a \cdot c$ ), ( $c \cdot a_1 \cdot b$ ), and ( $b \cdot a \cdot a$ ) by  $\Delta$ ,  $\Delta_1$ ,  $\Delta_2$  respectively,

$$k\Delta(c^3 - e^3) + k_1\Delta_1(b^3 - c^3) + k\Delta_2(a^3 - b^3) = pe^3 - p'a^3,$$

and this will be found consistent with the values of the dilatation supplied by (38), (39), and (40) for the three layers.

### *Summary.*

The principal results arrived at for the application of uniform surface-pressure are as follows :—

#### A.

(1) In any simple sphere or spherical shell, or in any one layer of a compound sphere or shell, there is a simple linear relation, independent of the elastic constants of the material, between the values of any the same stress or strain over any three concentric spherical surfaces.

#### B.

For the effects of altering a spherical layer so as to increase one or both of its elastic constants (the effects of diminishing one or both constants, generally speaking, being the exact opposite) :—

(2) The radial-pressure gradient falls off in steepness both inside and outside the altered layer, making up for this by increased steepness in the layer itself.

(3) The change of volume—whether expansion following internal pressure, or contraction following external pressure—is reduced in the material both inside and outside the altered layer.

(4) The altered layer itself suffers greater change of volume than if the entire sphere or shell were composed of the same material as the layer.

(5) The alteration of compressibility only throughout a layer of given volume is equally effective for all positions of the layer, but the alteration of rigidity only is more effective the nearer the altered layer to the centre.

(6) The stress-difference vanishes at every point of a simple solid sphere ; but, if the compressibility of a layer be altered, the stress-difference attains a finite value both outside the layer and in the material of the layer itself, becoming of importance in the layer itself however thin that may be.

## XIX. *Electrical Resonance and Electrical Interference.*

By JOHN TROWBRIDGE\*.

[Plate VII.]

THE solution of the differential equations which express the distribution of electricity on conductors of various forms and varying magnetic permeability is not always simple ; and many assumptions have been made in regard to the constants which enter these equations. Thus Poincaré † assumes that the spark of a vibrator is dampened more readily than that of the oscillator. This has been shown independently by Bjerknes to be true when the oscillating circuit is not closed by a spark-gap ‡. Stefan §, by making the assumption that the oscillations are confined to the outer layer of the conductor, reduced his differential equation to the form treated by Lord Kelvin, in periodic heat movements. Analysis leads him to suppose that the formula  $t = 2\pi \sqrt{LC}$  applies only to a special case ; and he gives a more general law.

With the conviction, therefore, that the experimental side

\* Communicated by the Author.

† *Electricité et Optique*.

‡ *Ann. der Physik und Chemie*, xlv. 1891 ; xlvii. 1892.

§ *Ibid.* xli. 1890.

of the subject should be more developed in order to decide, if possible, upon the truth of the various assumptions that have been made, I have continued my studies on the oscillations of electricity with the aid of more powerful methods of studying periodic currents than I had hitherto used. In a paper on the oscillations of lightning discharges \*, I expressed the opinion that the method first employed by Spottiswoode, of exciting a Ruhmkorff coil or transformer by means of an alternating-current dynamo, put in the hands of an experimenter a far more powerful method of studying electrical oscillations than the old method of charging Leyden jars by means of an electric machine, or by the use of a Ruhmkorff coil with a battery. I have, therefore, in this investigation, employed an alternating machine capable of giving 120 volts and a current of from 15 to 25 amperes, and have employed suitable transformers to obtain the necessary difference of potential to produce the sparks which I wished to study.

Generally I have employed one primary or exciting circuit between two entirely separate and disconnected resonating or secondary circuits. The image of the three sparks thus produced could then be compared upon the same plate.

Before entering into a more detailed account of the apparatus I employed, I will state the most striking results which I have obtained. A unidirectional spark (non-oscillatory) always excites an oscillatory discharge in a secondary circuit if the self-induction, capacity, and resistance of this secondary circuit permit an oscillatory movement. It is therefore not necessary that the spark in a primary circuit should be an oscillating one in order to excite oscillations in a neighbouring conductor. In this respect two electrical circuits are not in close analogy with two tuning-forks. It is difficult by a unidirectional movement of the prongs of one tuning-fork to excite the vibrations of another fork which is not in tune with the first fork. In every secondary circuit, or circuits neighbouring to the primary circuit, the first effect of the exciting unidirectional primary spark is to make the secondary circuits act as if there were no capacity in their circuits. In these circuits a thread-like spark results which is exactly like that produced when all the capacity in the secondary circuits is removed. After a short interval of time the electricity rushes into the condensers and begins to oscillate, the strength of the oscillations rising, after one or two vibrations, to a maximum and then decreasing; the rate of oscillation finally assumes a steady state, and is expressed by the formula  $t = 2\pi \sqrt{LC}$ .

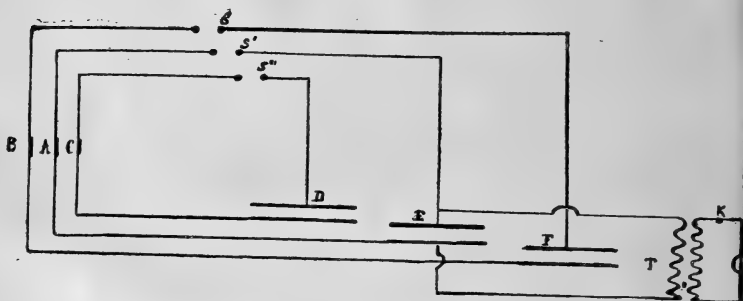
\* Phil. Mag. October 1893.

This formula, moreover, does not hold for the first instants. The electricity seems to be separated only along the wires at first, and the circuit vibrates more like a closed organ-pipe than an open one.

If a unidirectional primary spark excites oscillations in neighbouring circuits which are slightly out of tune, the phenomenon of electrical beats or interferences can be produced in these circuits, and can be shown by photography.

If the primary spark ceases to be unidirectional and is allowed to oscillate, the oscillations of the primary spark tend to compel those of the secondary or neighbouring circuits to follow them; if they are not sufficiently powerful to do this, they beat with the oscillation of the secondary circuit. Moreover, if all capacity is removed from the neighbouring circuits, they oscillate in tune with the primary circuit, following the latter exactly. The secondary circuits without capacity act like sensitive plates and exactly reproduce every disturbance in the primary oscillating circuit. Leaving for the end of this paper a more detailed account of my results, I will now describe my apparatus.

Fig. 1.



In fig. 1, S, S', S'' are three spark-gaps in the same vertical plane, but not immediately over each other, in order that the photographs may not overlap. B, A, C are three coils placed vertically on the same axis. These circular coils consisted of from one to four turns of well insulated wire. The mean radius of the coils was 915 centim. D, E, and F are the condensers respectively of the three independent circuits: these condensers were made of hard sheet-rubber 0.3 centim. thick; the coated surfaces could be varied by rolling up the layers of tinfoil which formed the coating. In certain cases air-condensers were substituted for the india-rubber condensers both for the condenser E of the primary circuit and for the condenser D of one of the secondary circuits. The air-condenser

employed for the primary circuit consisted of two large iron frames, upon which sheets of tin were screwed. The condenser-plates thus made were 210 centim. by 330 centim., and were placed 2 centim. apart. The air-condenser employed in the secondary circuit replacing at times the hard-rubber condenser D is described, together with the photographic apparatus, in a previous paper on *Electrical Oscillations*\*. It was placed in a room provided with yellow window-shades (orange fabric). It was found necessary also to construct a camera-box about 10 feet long, which extended from the spark-gap to the revolving mirror. This box was so constructed that the direct light of the sparks was shielded from the sensitive plate which was placed directly below the spark-gap. The plate thus received only the light thrown by the revolving mirror, which was placed at the opposite end of the camera-box. The operator, seated at the spark-end of this camera, closed for an instant a key K (woodcut, fig. 1) placed in the circuit of the alternator M. Looking through the film of the sensitive plate, one could determine when a suitable photograph had been taken; for the image of the sparks spread out by the revolving mirror could be clearly seen, the film acting like a ground-glass. It was thus possible to take a large number of photographs with the greatest ease, the rate of the alternator being so high that at each sudden make of the key several photographs could often be obtained at once upon the strips of sensitive plates, which were 25 centim. by 6 centim. It is evident that one of the circuits, for instance B, could be made a time-circuit. The self-induction and capacity in the circuit could be carefully determined and maintained constant. The formula  $t = 2\pi \sqrt{LC}$  could be thus printed, so to speak, on each negative. For this time-circuit I have employed a fine wire coil which was slipped upon the same electromagnet which formed the primary of the step-up transformer T. I had thus two step-up transformers with a common primary: one produced the sparks of the vibrator, the other the spark of the time-circuit.

In fig. 2 (Plate VII.) S' represents photographs of the unidirectional primary spark. S is the unidirectional spark produced in a neighbouring circuit B from which the capacity has been removed. S'' is the oscillating spark in the circuit C: the condenser of this circuit was an air-condenser. The spark S shows that no oscillation is concealed by the heavy pilot-spark of the exciting spark S'. The photographs S'' show that the unidirectional spark S' can

\* *Proc. Amer. Acad. Arts and Sciences*, May 28, 1890; *Phil. Mag.* [5] xxx. p. 323 (October 1890).

set the circuit C into oscillatory movement, and that this oscillatory movement continues long after the exciting blow has ceased. A careful study of many photographs of this nature shows that a circuit containing capacity and self-induction acts at the first instant as if no capacity were in the circuit. It then begins to oscillate with a higher period than it afterwards reaches, acting at first like a closed organ-pipe and subsequently like a pipe open at both ends.

In fig. 3, S' represents an oscillating primary discharge. S represents the photograph of the spark produced in the circuit B from which the capacity had been removed. The movements in this circuit B exactly follow those of the exciting circuit A. S'' is the photograph of the oscillating movement produced in the circuit C. It is of a different period from that of the exciting circuit S' and continues much longer. A secondary circuit without capacity acts like a sensitive plate, and accurately follows every movement of the exciting circuit.

In fig. 4 S' represents again the oscillating primary circuit, S the oscillating secondary circuit C. The circuits are nearly in geometrical resonance. Slight beats, however, can be observed. The duration of the secondary is nearly the same as that of the primary.

Fig. 5 shows clearly the phenomena of beats. In this case the secondary circuit was 20 centim. from the primary circuit.

Fig. 6 also shows the phenomenon of beats, and also the rise to a maximum in the oscillations of the secondary circuit, S. In this case an iron wire constituted a portion of circuit C. It seemed as if the effort to magnetize the iron diminished the power to produce the initial movement in the secondary circuit with as much energy as was the case when a copper wire of inductance equal to the iron wire was introduced in its place.

I have stated that Stefan \* has given a theory of electrical oscillations, and in his interpretation of his equation points out the necessity of supposing under certain conditions an aperiodic movement superimposed upon an oscillatory movement, in conductors containing self-induction and capacity. In regard to this latter point, my experiments seem to support his theoretical conclusions. I am inclined to believe, however, that the behaviour of condensers in secondary circuits, which are suddenly submitted to electrical disturbances, cannot properly be explained by the theory in Stefan's paper. Moreover, it results from his theory that electrical oscillations

\* *Ann. der Physik und Chemie*, xli. 1890, p. 422.

on an iron circuit of the same geometrical form and dimension as a copper circuit have the same period as oscillations on the copper circuit, supposing the capacity in the two circuits to be equal. I am led to suspect that there is a change of the period of electrical oscillations when an iron wire is substituted for a copper wire of the same geometrical form. I shall return to this subject of the change of period on iron wires in a following paper.

Oettingen\* has given some beautiful examples of the interference of electrical oscillations of different periods when they are led, so to speak, to the same spark-gap. I believe that my photographs are the first ones, however, which show the existence of such electrical beats or interference between independent circuits.

In order to present electrical beats between two secondary circuits both of which were excited by a unidirectional movement in a primary, I employed in certain cases two primary coils of one turn each, connected in series, and placed these primaries at right angles to each other; the secondaries corresponding to these two primaries were thus also at right angles to each other. This disposition of my apparatus enabled me to study the effect of two secondaries on each other; for on varying the angle between the planes of the primary coils and their accompanying secondaries, the beats can be made to appear or disappear.

It seems to me that we have in these photographs evidence of what may be termed the electrokinetic momentum of electricity. Something very like inertia is certainly shown by the gradual rise to a maximum and the behaviour of secondary circuits to unidirectional impulses from a primary circuit. A mental picture of the disturbance produced in secondary circuits can be produced in my mind by analogies drawn from the subject of the motion of fluids. In such analogies, to my mind, the idea of inertia is always present. I remarked in the opening of this paper that the formula  $t = 2\pi \sqrt{LC}$  does not apply at the instant of starting an oscillating current in a secondary conductor by means of a unidirectional flow in a primary circuit. This formula is true only after the full effect of the capacity of the oscillating circuit comes into play. My photographs show that at first neighbouring secondary circuits act like circuits without capacity, the oscillations in such circuits rise to a maximum in intensity and then fall, after the rate is established. This is true also when air-condensers are employed, and cannot therefore be attributed to the action of a solid or liquid dielectric.

\* *Ann. der Physik und Chemie*, xxxiv. 1888.

Bjerknes has shown\* that the oscillations in a Hertz resonator are not damped out so quickly as those in the primary exciting circuit. My photographs also show that the oscillations in all neighbouring circuits continue long after the unidirectional spark in the primary or exciting circuit has ceased. This is true whether there is resonance or not, and is more marked when the circuits are not in tune, except so far as electrical beats tend to damp the oscillations of the secondary circuit.

I am inclined to believe, therefore, that the conclusions of Bjerknes are true only for open circuits or circuits in which no sparks occur. When sparks occur in two circuits which are in resonance the duration of time-sparks appears to be the same. With periods ranging from  $\cdot 00001$  to  $\cdot 000001$  of a second, I have found it impossible to tune two circuits in which sparks occurred to perfect resonance. There were always indications of beats due, I believe, to the capacity not rising immediately to its full value.

The method which I have outlined in this paper seems to offer a fruitful one for investigation; for a large number of comparative photographs can be taken with far greater ease than by the arrangement of apparatus employed by Feddersen.

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XX. *The Attraction of Unlike Molecules.*—II. *The Surface-Tension of Mixed Liquids.* By WILLIAM SUTHERLAND†.

THE most direct method of measuring the attractions of unlike molecules seems to be by obtaining a theoretical expression for the surface-tension of mixed liquids involving the attractions of the unlike molecules of the liquids as well as the attractions of the like molecules for one another, and then by experimental determinations of the surface-tensions of mixtures to obtain the data wherewith to calculate the attractions of the unlike molecules from the theoretical expression. The present paper contains both a theoretical and an experimental part, of which the theoretical had better come first as indicating the lines on which the experiments are to be discussed.

In a paper on the Law of Molecular Force (Phil. Mag. [5] vol. xxvii. p. 305), which has been largely superseded by

\* *Ann. der Physik und Chemie*, xliv. 1891; xlvii. 1892.

† Communicated by the Author.



a later one on the Laws of Molecular Force (Phil. Mag. March 1893, [5] vol. xxxv. p. 211), there is given the establishment of an expression for the surface-tension of a liquid whose molecules attract one another with a force inversely as the fourth power of the distance between them. If  $3Am^2/r^4$  denotes the molecular attraction between two molecules of mass  $m$  at distance  $r$  apart in a liquid of density  $\rho$ , then it is shown that the surface-tension

$$\alpha \propto A\rho^2e, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $e$  is a length of the order of magnitude of the average distance of a molecule from its nearest neighbours and proportional to that distance; for it represents the distance to be left between two continuous distributions of matter on opposite sides of a plane in order that the attraction between them may be the same as that between two molecular distributions, the density and law of attraction in the continuous and molecular distributions being the same.

Suppose we have a gramme of a mixture of which a fraction  $p_1$  is a liquid of density  $\rho_1$  and molecular mass  $m_1$ , and the fraction  $p_2$  a liquid of density  $\rho_2$  and molecular mass  $m_2$ , producing a liquid of density  $\rho$ ; if there is no shrinkage on mixing the liquids 1 and 2, then

$$1/\rho = p_1/\rho_1 + p_2/\rho_2. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now in the mixture  $p_1$  grammes of liquid 1 are distributed through a volume  $1/\rho$ , and by themselves form a medium of density

$p_1\rho$ , to be denoted by  $\rho_1'$ ;

similarly the other liquid 2 has in the mixture a density

$p_2\rho$ , to be denoted by  $\rho_2'$ .

Thus, then, if we draw a plane in the mixed liquid and seek to represent the attraction between the molecules on the opposite sides of the plane, the problem reduces itself to that of finding the attraction between a liquid 1 of density  $\rho_1'$  on one side (say the left side) on the liquid 1 of density  $\rho_1'$  on the right side, and the similar attraction between the parts of liquid 2 of density  $\rho_2'$  on the left and right sides, and the attraction of liquid 1 of density  $\rho_1'$  on left on liquid 2 of density  $\rho_2'$  on right, and the attraction of liquid 2 of density  $\rho_2'$  on the left on liquid 1 of density  $\rho_1'$  on the right. The last two attractions are equal; thus in place of the expression  $A\rho^2e$  in the surface-tension of a single liquid we shall have for the mixture

$${}_1A_1\rho_1'^2e_1' + {}_2A_2\rho_2'^2e_2' + 2{}_1A_2\rho_1'\rho_2'e_1'e_2', \quad . \quad . \quad . \quad (3)$$

where  $e_1'$ ,  $e_2'$ , and  ${}_1e_2'$  are distances corresponding to  $e$  and representing the distances to be left between continuums which may be supposed to replace the molecular mediums whose attractions have just been enumerated. For a single liquid, for instance liquid 1 for which the value of  $e$  may be denoted by  $e_1$ ,  $e_1$  is proportional to  $(m_1/\rho_1)^{\frac{1}{3}}$ ; and then for its surface-tension relation (1) may be written

$$\alpha_1 = k {}_1A_1 \rho_1^2 (m_1/\rho_1)^{\frac{1}{3}}, \quad . \quad . \quad . \quad . \quad (4)$$

where  $k$  is the same for all liquids. Similarly for liquid 2,

$$\alpha_2 = k {}_2A_2 \rho_2^2 (m_2/\rho_2)^{\frac{1}{3}}. \quad . \quad . \quad . \quad . \quad (4)$$

Now if  $e_1$  is taken as represented by  $(m_1/\rho_1)^{\frac{1}{3}}$ , we cannot take  $e_1'$  as represented by  $(m_1/\rho_1')^{\frac{1}{3}}$ ; because if we did so and then in (3) put  $p_1 = p_2$  and suppose liquid 2 to become identical with liquid 1, in which case  $e_1' = e_2' = {}_1e_2'$ , we should find that (3) would not reduce to  ${}_1A_1 \rho_1^2 e_1$ , as it ought. The most appropriate way in which to represent  $e_1'$  is to take it as given by  $(m_1/\rho_1')^{\frac{1}{3}}$  reduced in the ratio of the cube root of the space  $p_1/\rho_1$  occupied by liquid 1 to the cube root of the total space  $1/\rho$ . Thus  $e_1'$  is represented by  $(m_1/\rho_1')^{\frac{1}{3}} (p_1 \rho / \rho_1)^{\frac{1}{3}}$ ,  $e_2'$  by  $(m_2/\rho_2')^{\frac{1}{3}} (p_2 \rho / \rho_2)^{\frac{1}{3}}$ , and  ${}_1e_2'$  by  $(e_1' + e_2')/2$ ; so that for the surface-tension of the mixture we get

$$\begin{aligned} {}_1\alpha_2 = k \left[ {}_1A_1 \rho_1'^2 \left( \frac{m_1 p_1 \rho}{\rho_1' \rho_1} \right)^{\frac{1}{3}} + {}_2A_2 \rho_2'^2 \left( \frac{m_2 p_2 \rho}{\rho_2' \rho_2} \right)^{\frac{1}{3}} \right. \\ \left. + 2 {}_1A_2 \rho_1' \rho_2' \left\{ \left( \frac{m_1 p_1 \rho}{\rho_1' \rho_1} \right)^{\frac{1}{3}} + \left( \frac{m_2 p_2 \rho}{\rho_2' \rho_2} \right)^{\frac{1}{3}} \right\} / 2 \right]; \quad (5) \end{aligned}$$

$$\begin{aligned} \therefore {}_1\alpha_2/\rho^2 = p_1^2 \alpha_1/\rho_1^2 + p_2^2 \alpha_2/\rho_2^2 \\ + \frac{{}_2A_2}{{}_1A_2} p_1 p_2 (\alpha_1 \alpha_2)^{\frac{1}{2}} \frac{(m_1/\rho_1)^{\frac{1}{3}} + (m_2/\rho_2)^{\frac{1}{3}}}{2 \{ (m_1/\rho_1)^{\frac{1}{3}} (m_2/\rho_2)^{\frac{1}{3}} \}^{\frac{1}{2}}}; \quad (6) \end{aligned}$$

which is an equation for determining the ratio  ${}_1A_2/({}_1A_1 {}_2A_2)^{\frac{1}{2}}$  by a measurement of the surface-tension of a mixture of the liquids 1 and 2 of known surface-tensions  $\alpha_1$  and  $\alpha_2$ . In these expressions, if we put  $p_1 = p_2 = 1/2$  and suppose liquid 2 to become identical with 1, we get the identity  ${}_1\alpha_1 = \alpha_1$  as we ought; also if we put  $p_2 = 0$  and  $p_1 = 1$  we get the same identity. There is doubtless something arbitrary in the manner in which we have fixed the values of  $e_1'$ ,  $e_2'$ , and  ${}_1e_2'$ , but we must remember that, in the original establishment of the relation  $\alpha = k A \rho^2 e$ , there is an arbitrary step in the

replacement of summation for separate molecules by integration for a continuum; the step is a piece of approximation whose justification is this, that even if we endeavoured to carry out the process of summation we should have to make arbitrary arrangements of the molecules. If we tried to sum for the molecules of a mixture, our suppositions as to the arrangement of the molecules would be still more markedly arbitrary; as, for instance, if we tried to represent the space-distribution of the spheres in a mixture of equal numbers of two sets of spheres of different sizes. These considerations seem to me to make the above expression for the surface-tension of a mixture satisfactory enough for present applications. When a higher degree of accuracy is required, it will be an interesting piece of mathematics to devise arrangements of molecules as in nature and convenient methods of summation.

In the paper on the Diffusion of Gases we have seen reason to believe that  ${}_1A_2 = ({}_1A_1{}_2A_2)$ ; and as the arithmetical mean of the molecular radii  $\{(m_1/\rho_1)^{\frac{1}{3}} + (m_2/\rho_2)^{\frac{1}{3}}\}/2$  of most pairs of liquids is little different from the geometrical mean  $\{(m_1/\rho_1)^{\frac{1}{3}}(m_2/\rho_2)^{\frac{1}{3}}\}^{\frac{1}{2}}$ , we can write approximately

$${}_1\alpha_2/\rho^2 = (p_1\alpha_1^{\frac{1}{3}}/\rho_1 + p_2\alpha_2^{\frac{1}{3}}/\rho_2)^2$$

as the law which rules the surface-tension of mixtures if  ${}_1A_2 = ({}_1A_1{}_2A_2)^{\frac{1}{2}}$ . But equation (6) is the fundamental one to be used in the discussion of the experiments, as it gives directly a value of  ${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$ , which is the thing sought in these investigations on the attraction of unlike molecules.

A fair amount of experimental work on the surface-tension of mixtures has been published, but hardly any of it is of immediate use in connexion with the present inquiry. For instance, Traube (*Ber. deut. chem. Ges.* xvii.; *Ann. der Chem.* cclxv.; *Journ. für prakt. Chem.* xxxiv.) has investigated the surface-tension of mixtures of water, and a large number of organic liquids such as alcohols, acids, and amines; but as water and the alcohols and acids are exceptional in their molecular structure in the liquid state, the surface-tensions of these mixtures cannot be appropriately discussed at the outset of this inquiry; but Traube's numerous experiments will doubtless be of great value when the exceptional nature of these substances is under systematic examination. But before Traube, Rodenbeck (*Wied. Beibl.* iv.) measured the rise in capillary tubes of a certain number of mixtures, of which only one set relates to strictly normal liquids, the

others involving the exceptional alcohol or complex petroleum. Before proceeding with an account of my own experiments on normal liquid pairs, I will illustrate the application of equation (6) to Rodenbeck's mixtures of the normal pair of liquids ethyl oxide and chloroform. The following table contains the data for the two liquids and five mixtures along with the value of  ${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$  calculated by equation (6) from the data for each mixture:—

	Ethyl Oxide.	Mixture. I.	Mixture. II.	Mixture. III.	Mixture. IV.	Mixture. V.	Chloro- form.
$p_1$ .....	1.0	.68	.44	.262	.125	.064	0.0
$p_2$ .....	0.0	.32	.56	.738	.875	.936	1.0
$\rho$ .....	.727	.870	1.020	1.170	1.320	1.400	1.494
$\alpha$ .....	1.83	2.01	2.22	2.44	2.52	2.60	2.78
${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$ .....		1.02	1.05	1.07	.97	.89	

In the table ethyl oxide is liquid 1 and chloroform is 2, and the surface-tensions are given in mgrms. weight per millim. The mean value of  ${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$  is 1.0; or, excluding mixtures IV. and V., in which the proportion of ethyl oxide is too small to favour an accurate value of  ${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$  from equation (6), the mean value is 1.05. Thus the theoretical formula (6) is proved to apply well to mixtures of ethyl oxide and chloroform, for which also  ${}_1A_2$  is proved to be equal to  $({}_1A_1{}_2A_2)^{\frac{1}{2}}$ .

Two other sets of Rodenbeck's experiments may be discussed here, although they relate to mixtures involving petroleum, which is itself a mixture, for the equation

$${}_1\alpha_2/\rho^2 = (p_1\alpha_1^{\frac{1}{2}}/\rho_1 + p_2\alpha_2^{\frac{1}{2}}/\rho_2)$$

can be generalized so as to apply to any mixture of any number of liquids. Suppose a gramme of any such mixture to contain  $p_1, p_2, p_3 \dots$  gramme of liquids 1, 2, 3 ..., and have a density  $\rho$  and surface-tension  $\alpha$ , then

$$\alpha/\rho^2 = (p_1\alpha_1^{\frac{1}{2}}/\rho_1 + p_2\alpha_2^{\frac{1}{2}}/\rho_2 + p_3\alpha_3^{\frac{1}{2}}/\rho_3 + \dots)^2.$$

If the liquids 2, 3, 4 ... in proportions  $p_2, p_3, p_4 \dots$  are supposed to form a separate liquid  $n$ , as for instance Rodenbeck's petroleum, then

$$\alpha/\rho^2 = \{p_1\alpha_1^{\frac{1}{2}}/\rho_1 + (p_2 + p_3 + \dots)\alpha_n^{\frac{1}{2}}/\rho^n\}^2;$$

so that the law for a mixture of mixtures is the same as for a mixture of pure liquids, and we ought to be able to apply equation (6) to a mixture of mixtures. Thus we can utilize Rodenbeck's measurements on mixtures of rectified petroleum and chloroform, and also of ordinary petroleum and ethyl

oxide, treating the petroleum as a single liquid. Arranging the data and results as before, we have :—

	Rectified petroleum.	Mixture I.	Mixture II.	Mixture III.	$\text{CHCl}_3$ .
$p_1$ .....	1.0	.633	.378	.1575	0.0
$p_2$ .....	0.0	.367	.622	.8425	1.0
$\rho$ .....	.767	.934	1.100	1.300	1.494
$\alpha$ .....	2.59	2.73	2.82	2.80	2.78
${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}} \dots$		1.1	1.11	1.06	

	Ordinary petroleum.	Mixture I.	Mixture II.	$(\text{C}_2\text{H}_5)_2\text{O}$ .
$p_1$ .....	1.0	.723	.461	0.0
$p_2$ .....	0.0	.277	.539	1.0
$\rho$ .....	.803	.780	.760	.727
$\alpha$ .....	2.66	2.41	2.22	1.83
${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}} \dots$		.96	.99	

In these cases the theoretical formula (6) is again verified by the approximate constancy of  ${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$ , and again the ratio  ${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$  has values close to 1.

In my own experiments the method adopted for measuring surface-tensions was by means of the rise in capillary tubes, but carried out in a special manner. Elsworth (Journ. Chem. Soc. liii.) suggested inclining the capillary tube at a large angle to the vertical, say  $\theta$ , so that a liquid which would rise a height  $h$  in the tube when vertical, while still rising only  $h$  vertically, in the inclined tube rises a distance  $h/\cos \theta$  measured along the tube; so that the accuracy of reading is increased in the ratio 1 to  $\cos \theta$ . It seemed to me that the best way to take advantage of this method for a number of liquids was to engrave a fixed mark on the tube, and then in each case to vary the inclination till the liquid rose as nearly as possible to the mark, reading the inclination in each case. The advantage of this method is that it makes one almost independent of variation in the bore of the capillary tube. It would have improved the accuracy of the method if a fine scale had been engraved on the tube near the fixed mark, so that one could read in each case the small departure from the fixed mark and allow for it in the calculations, but this was not done. The capillary tube was fitted tightly into one leg of a V-tube of 6 millim. internal diameter, the joint being protected by a piece of india-rubber tube slipped over it: the angle of the V was such that the other leg was nearly vertical in the experiments with most liquids. A second mark was engraved on the capillary a little above where it entered the V-tube, and at a distance of 184 millim. from the other fixed mark; the level of the free surface of the liquid in the V-tube

was always brought to the level of this second mark, so that the length of the column raised by capillary action in the tube was always 184 millim. The open limb of the V-tube was provided with a loose cork to prevent evaporation. The capillary tube was clamped to a wooden lath hinged at one end to a stand, and provided at the other end with an index whose terminal point was 610 millim. from the hinge, and to the lath was hinged a wooden piece by which it could be supported at any angle. Instead of reading the angle of inclination of the lath and its attached tube, I read on a vertical scale the height of the index above the point indicated by it when the tube was lowered to a horizontal position. The readings thus obtained were accordingly directly proportional to the capillary heights. In the case of water at  $15^{\circ}$  C. the reading was 196 millim.; and as the mean result of previous experimenters is that at  $15^{\circ}$  C. in a tube of 1 millim. radius water rises 14.9 millim., it was only necessary for me to multiply my readings for various liquids and mixtures at  $15^{\circ}$  (really  $14^{\circ}$  to  $16^{\circ}$ ) by  $14.9/196$  to obtain the capillary height  $h$  as usually given, namely, number of millim. rise in a tube of 1 millim. radius.

The chief objection that I found to the method of experimenting was that I had two adjustments to make that depended on one another, namely, that of the level of the liquid in the wide tube and the level of the liquid in the capillary tube. In any further experiments I will take steps to make these two independent of one another.

The capillary tube and the liquids (except chloroform) in a state of sufficient chemical purity were given to me by Mr. W. Percy Wilkinson, analyst, of Melbourne. The following are the capillary heights  $h$  of the separate liquids in millim. in a tube of 1 millim. radius, their densities  $\rho$  and their surface-tensions  $\alpha = h\rho/2$  all at  $15^{\circ}$  C.

	Water, $\text{H}_2\text{O}$ .	Ethyl oxide, $(\text{C}_2\text{H}_5)_2\text{O}$ .	Carbon di- sulphide, $\text{CS}_2$ .	Acetone, $(\text{CH}_3)_2\text{CO}$ .	Methyl iodide, $\text{CH}_3\text{I}$ .	Amyl acetate, $\text{CH}_3\text{CO}_2\text{C}_5\text{H}_{11}$ .	Ethyl, acetate, $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ .
$h$ .....	14.9	5.4	5.7	6.4	3.3	6.2	5.9
$\rho$ .....	1.0	.723	1.269	.802	2.29	.879	.902
$\alpha$ .....	7.45	1.95	3.6	2.55	3.8	3.5	2.7

	Ethyl aceto- acetate, $\text{C}_6\text{H}_{10}\text{O}_3$ .	Chloroform, $\text{CHCl}_3$ .	Benzene, $\text{C}_6\text{H}_6$ .	Nitro- benzene, $\text{C}_6\text{H}_5\text{NO}_2$ .	Anilin, $\text{C}_6\text{H}_5\text{NH}_2$ .	Dimethyl- anilin, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ .
$h$ .....	6.9	4.0	7.3	7.9	8.9	7.9
$\rho$ .....	1.017	1.484	.878	1.209	1.030	.955
$\alpha$ .....	3.5	3.0	3.2	3.25	4.6	3.8

In working with mixtures of these liquids the general procedure was to make three mixtures in the proportions of

about 3 or 2 to 1, 1 to 1, and 1 to 2 or 3 parts by weight of the two liquids, to measure the capillary height of each mixture immediately after it was made, and then to measure the density. In some cases where one of the liquids was very volatile, and for any reason the level of the liquid in the V-tube took longer than usual to adjust, so that the cork was off too long, evaporation of the volatile ingredient altered the proportions of the two ingredients a little from their original values and altered the specific gravities a little. On account of this occasional source of error, the values of  $p_1$  and  $p_2$  will be given only to two figures, though measured to three; as  $p_1 + p_2 = 1$ , it is necessary to give only  $p_2$ .

## Mixtures with ethyl oxide as liquid 1.

2.		$p_2$ .	$\rho$ .	$h$ .	$a$ .	${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$ .	
						.8	Mean.
OS <sub>2</sub> . .....	I.	.19	.791	5.2	2.07	.8	.9
	II.	.28	.826	5.2	2.15	.9	
	III.	.43	.893	5.1	2.28	.9	
	IV.	.73	1.063	5.1	2.71	.8	
	V.	.83	1.122	5.2	2.92	.8	
(CH <sub>3</sub> ) <sub>2</sub> CO.	I.	.32	.748	5.7	2.13	1.0	1.0
	II.	.58	.763	5.8	2.21	1.0	
	III.	.84	.787	6.1	2.40	1.0	
CH <sub>3</sub> I.....	I.	.33	.937	4.5	2.11	.9	.9
	II.	.52	1.165	4.1	2.39	.9	
	III.	.72	1.430	3.7	2.64	.9	
CH <sub>3</sub> CO <sub>2</sub> C <sub>5</sub> H <sub>11</sub> .	I.	.40	.777	5.5	2.14	.9	.9
	II.	.52	.801	5.6	2.24	.9	
	III.	.82	.844	6.1	2.58	1.0	
CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> .	I.	.37	(.798)	5.5	2.20	1.0	1.0
	II.	.51	.807	5.5	2.22	.9	
	III.	.73	.844	5.7	2.40	1.0	
C <sub>6</sub> H <sub>10</sub> O <sub>3</sub> .	I.	.30	.817	5.4	2.21	.8	.9
	II.	.50	.867	5.5	2.38	1.0	
CHCl <sub>3</sub> .....	I.	.54	.998	4.8	2.39	1.1	1.1
C <sub>6</sub> H <sub>6</sub> .....	I.	.22	.752	5.7	2.14	1.0	1.0
	II.	.53	.798	6.5	2.59	1.1	
	III.	.79	.840	6.6	2.77	.9	
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> .	I.	.48	.938	5.7	2.67	.7	
	II.	.68	(1.033)	5.8	2.98	.6	
	III.	.80	1.089	5.9	3.21	.4	
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> .	I.	.44	.850	5.9	2.51	.7	.7
	II.	.52	.879	6.2	2.73	.7	
	III.	.74	.934	6.5	3.03	.6	
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> .	I.	.32	(.796)	5.6	2.23	.8	.8
	II.	.48	.832	5.9	2.45	.8	
	III.	.53	.849	6.0	2.55	.8	
	IV.	.68	.880	6.2	2.73	.7	

## Mixtures with carbon disulphide as liquid 1.

2.		$p_2$ .	$\rho$ .	$h$ .	$a$ .	${}_1A_2/({}_1A_1{}_2A_2)^{\frac{1}{2}}$ .	
$(CH_3)_2CO$ .	I.	·44	1·000	5·6	2·80	·9	·9
	II.	·51	(·979)	5·8	2·84	·9	
	III.	·61	·923	6·0	2·77	1·0	
$CH_3I$ .....	I.	·32	1·496	4·8	3·61	·9	
	II.	·43	1·603	4·4	3·52	·8	
	III.	·55	(1·716)	3·8	3·19	·6	
$CH_3CO_2C_5H_{11}$	I.	·26	1·124	5·8	3·26	1·0	1·0
	II.	·53	1·003	5·9	2·96	1·0	
	III.	·82	·920	6·3	2·90	1·1	
$CH_3CO_2C_2H_5$ .	I.	·42	1·084	5·5	2·98	·9	·9
	II.	·71	·984	5·7	2·80	·9	
	III.	·90	(·929)	5·8	2·69	·9	
$CHCl_3$ .....	I.	·82	(1·441)	4·3	3·10	1·0	1·0
$C_6H_{10}O_3$ ....	I.	·36	(1·164)	5·8	3·37	·9	·9
	II.	·51	1·104	6·1	3·36	1·0	
	III.	·67	1·072	6·2	3·32	·9	
$C_6H_8$ .....	I.	·23	1·148	6·0	3·44	1·0	1·1
	II.	·51	1·028	6·7	3·44	1·1	
	III.	·69	·966	7·0	3·38	1·1	
$C_6H_5NO_2$ .	I.	·16	1·260	6·0	3·78	1·0	·9
	II.	·40	1·242	6·5	4·04	1·0	
	III.	·58	1·230	6·4	3·94	·8	
$C_6H_5NH_2$ .	I.	·20	1·202	6·4	3·85	1·0	1·0
	II.	·56	1·123	7·2	4·04	·9	
	III.	·78	1·072	8·1	4·33	1·0	
$C_6H_5N(CH_3)_2$	I.	·21	1·168	6·4	3·73	1·1	1·1
	II.	·44	1·093	6·9	3·78	1·1	
	III.	·72	1·012	7·1	3·59	1·0	

## Mixtures with chloroform as liquid 1.

$C_6H_6$ .....	I.	·48	(1·115)	5·8	3·23	1·1	1·1
$C_6H_5NH_2$ .....	I.	·54	(1·198)	6·3	3·78	·9	·9
$C_6H_{10}O_3$ .....	I.	·34	(1·283)	5·3	3·40	1·1	1·1

## Mixtures with benzene as liquid 1.

$C_6H_5NH_2$ .....	I.	·46	(·942)	7·6	3·58	·9	·9
$CH_3CO_2C_5H_{11}$ ...	I.	·15	(·878)	7·0	3·07	·9	·9

## Mixtures with anilin as liquid 1.

$C_6H_5NO_2$ .....	I.	·32	(1·081)	8·6	4·64	1·0	1·0
$CH_3CO_2C_2H_5$ .....	I.	·39	(·977)	7·2	3·52	·9	·9

The densities enclosed in brackets were not observed, but calculated from the densities of other mixtures or of the component liquids on the supposition of no shrinkage in mixing.



Of the 28 pairs of liquids examined, 24 show a value of the ratio  ${}_1A_2/({}_1A_{12}A_2)^{\frac{1}{2}}$  lying between .9 and 1.1, while of the remaining 4, 2 (ethyl oxide and anilin and ethyl oxide and dimethylanilin) show what appears to be a constant value of the ratio having in one case the value .7 and in the other .8; in the other two cases, namely, those of ethyl oxide and dimethyl anilin and carbon disulphide and methyl iodide, the theoretical equation (6) does not apply as the value of  ${}_1A_2/({}_1A_{12}A_2)^{\frac{1}{2}}$  is not constant for different values of  $p_1$ . Some mixtures of ethyl oxide and  $CS_2$  gave a precipitate disappearing only with shaking; so that perhaps they ought not to rank as genuine mixtures of two liquids. We will not enquire at present more closely into these exceptional cases, nor discuss the great class of exceptions formed by watery solutions and mixtures. In the "Laws of Molecular Force" the method of treating watery solutions was pointed out, and the method will be improved and developed in another paper devoted to the surface-tensions of watery solutions alone. As to watery mixtures it will suffice to instance as the most extreme case of exceptional capillary behaviour the well-known one of mixtures of water and amyl alcohol, water with a surface-tension of 7.4 when mixed with only 2.5 per cent. of amyl alcohol having a surface-tension of 3.7 has its surface-tension reduced to 2.8, which is even lower than that of the small amount of added alcohol. It is clear that cases of this sort are complicated with quite another class of phenomena from those we are discussing in connexion with normal liquid mixtures, and that we have a right to set them apart for separate study.

The result  ${}_1A_2 = ({}_1A_{12}A_2)^{\frac{1}{2}}$ , which is the outcome of this investigation on the attraction of unlike molecules, has an important bearing on the interpretation of the data as to the attraction of like molecules contained in the "Laws of Molecular Force;" for evidently the expression  $Am^2$  for the attraction of two like molecules must be regarded as the product of two parameters  $A^{\frac{1}{2}}m$  characteristic of each molecule. The investigation of the attraction of like molecules from this point of view will be taken up in my next paper, "Further Studies on Molecular Force."

Melbourne, January 1894.

XXI. *On Electromagnetic Induction in Plane, Cylindrical, and Spherical Current-Sheets, and its Representation by Moving Trails of Images.* By G. H. BRYAN, M.A.\*

PART I.—GENERAL EQUATIONS—PLANE SHEETS.

*Introduction.*

1. IT is well known that if a very thin, indefinitely extended plane sheet of metal of finite conductivity is placed in a varying magnetic field due to the presence of moving magnetic poles in its neighbourhood, induction-currents are set up in the sheet and the field of force due to these currents may be represented by a moving trail of images.

In the present paper the surface-conditions which hold at the surface of a plane, cylindrical, spherical, or other conducting sheet of uniform small thickness are deduced directly from the fundamental laws of electromagnetic induction. By working directly with the scalar magnetic potential, and avoiding the introduction of the vector potential and the quantity which Maxwell denotes by  $P$ , the investigations are much simplified. Moreover, in at least one comparatively recently published paper the boundary conditions satisfied by the vector potential at the surface of separation of two different media have been erroneously stated, and for this reason it is advantageous to employ a method which obviates the difficulty.

The results will be employed to show how the field due to the presence of a magnetic pole of varying intensity in the neighbourhood of a plane, cylindrical, or spherical current-sheet may be represented by means of a moving trail of images. By the principle of superposition the effect of any number of poles of varying intensity can be deduced, and the corresponding expressions for the field can thus be obtained when the variable inducing system of magnets is of the most general possible character, as, for example, one (or more) magnetic poles moving about in any manner whatever.

In this way a synthetic solution of the problem of induction in current sheets is obtained. The phenomena of induction in spherical and other current sheets have been treated at considerable length from an analytical point of view by Larmor, Lamb, and Niven, and the last-named writer has made some attempt, in the case of a sphere, to interpret the results by means of images; but the present investigation

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seemed desirable for many reasons, and it is hoped that it will overcome some of the difficulties, and elucidate some of the obscurities which present themselves in most treatments of this interesting application of the principles of electromagnetism.

*Fundamental Assumptions.*

2. The laws of electromagnetic induction assert that in bodies at rest

I. *The total current across any enclosed portion of a surface which always contains the same particles is equal to  $1/4\pi$  of the line-integral of magnetic force round the curve bounding the surface.*

II. *The rate of decrease of the surface-integral of magnetic induction across any enclosed surface which always contains the same particles is equal to the line-integral of electromotive force round the curve bounding the surface.*

In applying these laws to an infinite dielectric separated into two portions by a thin conducting sheet, it is usually assumed that the disturbance produced by the inducing system is not a very rapidly alternating one, so that displacement currents in the dielectric have no appreciable magnetic effect\*. With this assumption, the magnetic force in the dielectric will always be derivable from a potential which will only depend on the inducing system and the currents in the sheet. In other words, the state of the dielectric will be given by an "equilibrium theory."

It is also assumed that the induction-currents at any point distribute themselves uniformly throughout the thickness of the sheet. This requires that the disturbance shall not be a very rapidly alternating one, and also that the thickness of the sheet shall be very small compared with the other linear dimensions of the system (such as the distances of the moving poles, the radius of the sheet if spherical, &c.).

*Surface Conditions at a Plane-Current Sheet.*

3. Let the plane of the sheet be taken as the plane of  $x, y$ , let the thickness of the sheet be  $c$ , and specific conductivity  $C$ .

Let  $\Omega_1, \Omega_2$  be the magnetic potentials on the negative and positive side of the sheet respectively,  $\phi$  the current function in the sheet at any point. Apply Law I. to the circuit formed by going along the positive side of the sheet from the origin to any point and returning along the negative side from that

\* Watson and Burbury, 'Mathematical Theory of Electricity and Magnetism,' ii, § 405.

point to the origin. Since the thickness of the sheet is small, the terms contributed to the line-integral of the magnetic force by the passage of the circuit from one side of the sheet to the other may be neglected and we obtain \*

$$\Omega_2 - \Omega_1 = 4\pi\phi + \text{constant.} \quad . \quad . \quad . \quad (1)$$

Now apply Law II. to any circuit  $s$  drawn in the plane of the sheet. Let  $S_1, S_2$  be two surfaces drawn in the dielectric infinitely near to the positive and negative faces of the sheet respectively and both bounded by the curve  $s$ , and let  $P, Q$  be the components of electromotive force at any point. Then, assuming the magnetic permeability of the dielectric to be unity, we have

$$\int (Pdx + Qdy) \text{ round } s = \frac{d}{dt} \iint \frac{d\Omega_1}{dz} dS_1 = \frac{d}{dt} \iint \frac{d\Omega_2}{dz} dS_2,$$

and since corresponding elements of the near surfaces  $S_1, S_2$  are equal, it is evident that

$$\frac{d\Omega_1}{dz} = \frac{d\Omega_2}{dz} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

at the surface, so that the normal component of magnetic induction is continuous, as it should be †.

Again, the equations of conduction give

$$C_c P = \frac{d\phi}{dy}, \quad C_c Q = -\frac{d\phi}{dx}.$$

Hence

$$\begin{aligned} \frac{d}{dt} \iint \frac{d\Omega_1}{dz} dS &= \frac{d}{dt} \iint \frac{d\Omega_2}{dz} dS = \frac{1}{C_c} \int \left( \frac{d\phi}{dy} \frac{dx}{ds} - \frac{d\phi}{dx} \frac{dy}{ds} \right) ds \\ &= -\frac{1}{C_c} \int \left( \frac{d\phi}{dy} \frac{dy}{dn} + \frac{d\phi}{dx} \frac{dx}{dn} \right) ds = -\frac{1}{C_c} \int \frac{d\phi}{dn} ds \\ &= -\frac{1}{C_c} \iint \left( \frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} \right) dS, \end{aligned}$$

where  $dn$  is the element of the outward-drawn normal to  $s$  and the surface-integral taken over the area  $S$  of the sheet bounded by the curve  $s$ .

\* Maxwell, 'Electricity and Magnetism,' ii. § 653.

† The magnetic permeability of the sheet itself will not affect the conditions of the problem unless it is required to proceed to a higher order of approximation by taking into account first powers of the thickness (or unless the sheet is formed of soft iron whose magnetic permeability may be large).

Hence at the surface of the sheet

$$\begin{aligned}\frac{d}{dt} \frac{d\Omega_1}{dz} &= \frac{d}{dt} \frac{d\Omega_2}{dz} \\ &= -\frac{1}{Cc} \left( \frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} \right) \\ &= -\frac{1}{4\pi Cc} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) (\Omega_2 - \Omega_1) \quad \text{by (1)} \\ &= \frac{1}{4\pi Cc} \frac{d^2}{dz^2} (\Omega_2 - \Omega_1) \quad . . . . . (3)\end{aligned}$$

(remembering that  $\nabla^2\Omega_1=0$  and  $\nabla^2\Omega_2=0$ ).

4. Now let  $\Omega_0$  be the magnetic potential due to the external or inducing system,  $\Omega'$  and  $\Omega''$  the magnetic potentials on the two sides due to the sheet itself, so that

$$\Omega_1 = \Omega_0 + \Omega', \quad \Omega_2 = \Omega_0 + \Omega'' \quad . . . . (4)$$

Then  $\Omega_0$  and its differential coefficients with respect to  $z$  are continuous in crossing the sheet, while from the symmetry of the field due to the sheet

$$\Omega'(x, y, z) = -\Omega''(x, y, -z), \quad . . . (5)$$

so that

$$\frac{d^n \Omega'}{dz^n} = (-1)^{n+1} \frac{d^n \Omega''}{dz^n}.$$

Therefore the surface condition (3) gives

$$\frac{d}{dt} \frac{d\Omega'}{dz} + \frac{d}{dt} \frac{d\Omega_0}{dz} = -\frac{1}{2\pi Cc} \frac{d^2\Omega'}{dz^2}, \quad . . . (6)$$

$$\frac{d}{dt} \frac{d\Omega''}{dz} + \frac{d}{dt} \frac{d\Omega_0}{dz} = +\frac{1}{2\pi Cc} \frac{d^2\Omega''}{dz^2} \quad . . . (7)$$

as the surface conditions satisfied by the potential at the two sides of the sheet.

### Surface Conditions at a Cylindrical Sheet.

5. Using cylindrical coordinates, let  $r=a$  be the equation of the middle surface of a cylindrical current-sheet, and let its thickness  $c$  be so small that the corresponding elements of its bounding surfaces and middle surface, viz.

$$(a - \frac{1}{2}c) d\theta dz, (a + \frac{1}{2}c) d\theta dz, \text{ and } a d\theta dz$$

are to be regarded as equal.

If  $\Omega_1, \Omega_2$  are the magnetic potentials inside and outside the

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sheet, we shall still have as for a plane sheet

$$\Omega_2 - \Omega_1 = 4\pi\phi + \text{constant}, \quad . \quad . \quad . \quad (1)$$

and by application of the second law to the small circuit bounding the surface-element  $a d\theta dz$ , we have at the sheet

$$\begin{aligned} \frac{d}{dt} \frac{d\Omega_1}{dr} &= \frac{d}{dt} \frac{d\Omega_2}{dr} = -\frac{1}{Cc} \left\{ \frac{d}{rd\theta} \frac{d\phi}{rd\theta} + \frac{d^2\phi}{dz^2} \right\} \\ &= -\frac{1}{4\pi Cc} \left\{ \frac{1}{r^2} \frac{d^2}{d\theta^2} + \frac{d^2}{dz^2} \right\} (\Omega_2 - \Omega_1) \\ &= \frac{1}{4\pi Cc} \left( \frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} \right) (\Omega_2 - \Omega_1), \end{aligned}$$

or

$$\frac{d}{dt} \left( r \frac{d\Omega_1}{dr} \right) = \frac{d}{dt} \left( r \frac{d\Omega_2}{dr} \right) = \frac{1}{4\pi Cc} \frac{d}{dr} r \frac{d}{dr} (\Omega_2 - \Omega_1). \quad . \quad . \quad (8)$$

#### *Surface Conditions at a Spherical Sheet.*

6. In the case of a spherical sheet of small thickness, we obtain in like manner

$$\frac{d}{dt} \frac{d\Omega_1}{dr} = \frac{d}{dt} \frac{d\Omega_2}{dr} = \frac{1}{4\pi Cc} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) (\Omega_2 - \Omega_1),$$

or

$$\frac{d}{dt} \left( r^2 \frac{d\Omega_1}{dr} \right) = \frac{d}{dt} \left( r^2 \frac{d\Omega_2}{dr} \right) = \frac{1}{4\pi Cc} \frac{d}{dr} r^2 \frac{d}{dr} (\Omega_2 - \Omega_1). \quad (9)$$

#### *Extension to Curved Sheets of other Forms.*

7. When the sheet is of any form other than those above considered, it is necessary to assume a certain law of variation of the thickness in order to put the boundary conditions into a form similar to those given above\*.

Let us use orthogonal coordinates  $\alpha, \beta, \gamma$ ; let the line-element be given by

$$ds^2 = \frac{d\alpha^2}{h_1^2} + \frac{d\beta^2}{h_2^2} + \frac{d\gamma^2}{h_3^2},$$

and let the equation of the current sheet be

$$\gamma = \text{constant}.$$

Equation (1) still holds, and by applying Law II. to the circuit enclosed on the sheet by the curves  $\alpha, \alpha + \delta\alpha, \beta$  and

\* Compare Watson and Burbury, §426.

$\beta + \delta\beta$ , we have the surface-condition

$$\begin{aligned} \frac{1}{h_1 h_2} \frac{d}{dt} h_3 \frac{d\Omega_1}{d\gamma} &= \frac{1}{h_1 h_2} \frac{d}{dt} h_3 \frac{d\Omega_2}{d\gamma} \\ &= -\frac{d}{d\alpha} \left\{ \frac{h_1}{Cch_2} \frac{d\phi}{d\alpha} \right\} - \frac{d}{d\beta} \left\{ \frac{h_2}{Cch_1} \frac{d\phi}{d\beta} \right\} \\ &= -\frac{1}{4\pi} \left\{ \frac{d}{d\alpha} \left( \frac{h_1}{Cch_2} \frac{d}{d\alpha} \right) + \frac{d}{d\beta} \left( \frac{h_2}{Cch_1} \frac{d}{d\beta} \right) \right\} (\Omega_2 - \Omega_1). \quad (10) \end{aligned}$$

But Laplace's equation which is satisfied by  $\Omega_1 \Omega_2$  may be written

$$\frac{d}{d\alpha} \left( \frac{h_1}{h_2 h_3} \frac{d\Omega}{d\alpha} \right) + \frac{d}{d\beta} \left( \frac{h_2}{h_3 h_1} \frac{d\Omega}{d\beta} \right) + \frac{d}{d\gamma} \left( \frac{h_3}{h_1 h_2} \frac{d\Omega}{d\gamma} \right) = 0.$$

Hence it is possible to eliminate differential coefficients with respect to  $\alpha, \beta$  from the surface-condition if, and only if,

$$Cc \propto h_3. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Hence the thickness of the sheet at any point must be inversely proportional to the distance between two neighbouring surfaces of the family  $\gamma = \text{constant}$  at that point. In the case of an ellipsoidal sheet this leads to the well-known condition that the thickness must be proportional to the perpendicular on the tangent-plane, or that the sheet must be a shell bounded by similar and similarly situated ellipsoids.

Writing

$$R = \frac{h_3}{2\pi Cc}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

the surface-condition now becomes

$$\frac{d}{dt} \left( \frac{h_3}{h_1 h_2} \frac{d\Omega_1}{d\gamma} \right) = \frac{d}{dt} \left( \frac{h_3}{h_1 h_2} \frac{d\Omega_2}{d\gamma} \right) = \frac{R}{2} \frac{d}{d\gamma} \left\{ \frac{h_3}{h_1 h_2} \frac{d}{d\gamma} (\Omega_2 - \Omega_1) \right\} \quad (13)$$

### *Synthetic Determination of the Images in a Plane Sheet.*

8. In order to illustrate the synthetic method, consider its application to the well-known case of a plane-current sheet. Let the induced currents be excited by a magnetic pole placed at the fixed point  $(x_0, y_0, z_0)$  on the positive side of the sheet whose strength is  $f(t)$  an arbitrary function of the time. Then

$$\Omega_0 = \frac{f(t)}{\{(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2\}^{\frac{1}{2}}}, \quad . \quad . \quad (14)$$

and the surface-condition satisfied by  $\Omega'$  the potential on

$$\frac{d^2\Omega'}{dzdt} + R\frac{d^2\Omega}{dz^2} = -\frac{d^2\Omega_0}{dzdt}, \quad \dots \quad (15)$$

where

$$R = \frac{1}{2\pi Cc}. \quad \dots \quad (16)$$

Integrating (15), the value obtained for  $\Omega'$  is found to be the potential due to magnetic poles or images on the positive side of the sheet, and these are outside the region over which the solution is required to hold, as they should be. We have

$$\begin{aligned} \left(\frac{d}{dt} + R\frac{d}{dz}\right)\Omega' &= -\frac{f'(t)}{\sqrt{\{(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2\}}}, \\ \therefore \Omega' &= -\int_{-\infty}^t e^{-R(t-\tau)} \frac{d}{dz} \frac{f'(\tau)}{\sqrt{\{(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2\}}} d\tau \\ &= -\int_{-\infty}^t \frac{f'(\tau)}{\sqrt{\{(x-x_0)^2 + (y-y_0)^2 + (z-z_0-Rt+R\tau)^2\}}} d\tau \\ &= -\frac{f(t)}{\sqrt{\{(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2\}}} \\ &+ \int_{-\infty}^t Rf(\tau) \frac{d}{dz} \frac{1}{\sqrt{\{(x-x_0)^2 + (y-y_0)^2 + (z-z_0-Rt+R\tau)^2\}}} d\tau. \end{aligned}$$

The first term represents the effect of a pole equal and opposite to the given pole at the point  $(x_0, y_0, z_0)$ , while the second term shows that the effect of the action of the pole between the times  $\tau$  and  $\tau + \delta\tau$  is represented at time  $t$  by a magnet of strength  $Rf(\tau)\delta\tau$  situated at the point  $(x_0, y_0, z_0 + R(t-\tau))$ . The potential at the positive side is found from the relation (5), or

$$\Omega''(x, y, z) = -\Omega'(x, y, -z).$$

When the pole is in motion the results thus arrived at enable us to plot out the moving images contributed during every time element  $\delta\tau$  of the motion in the well-known way, or they may be obtained as follows:—

9. If, instead of a single magnetic pole, we are dealing with a magnetic distribution on the positive side of the sheet such that the volume-density of magnetism of the point  $(x_0, y_0, z_0)$  is  $F(x_0, y_0, z_0, t)$ , we must write  $F(x_0, y_0, z_0, t) dx_0 dy_0 dz_0$  for  $f(t)$  in the expressions for  $\Omega_0$  and  $\Omega'$ . Hence we have



$$\Omega_0 = \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{F(x_0 y_0 z_0 t) dx_0 dy_0 dz_0}{\{(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2\}^{\frac{3}{2}}}, \quad (18)$$

$$\Omega' = -\Omega_0 - \int_{-\infty}^t d\tau \int_0^\infty dz_0 \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{R F(x_0 y_0 z_0 \tau)}{z-z_0-R(t-\tau)} dx_0 dy_0. \quad (19)$$

If now the inducing system consists of a single pole of strength  $f(t)$  which moves about in any manner so that its coordinates at any time  $t$  are  $\xi(t)$ ,  $\eta(t)$ ,  $\zeta(t)$ , functions of  $t$ , we have

$$F(x_0 y_0 z_0 \tau) = 0,$$

except when  $x_0 = \xi(\tau)$ ,  $y_0 = \eta(\tau)$ ,  $z_0 = \zeta(\tau)$ , and then

$$F(x_0 y_0 z_0 \tau) dx_0 dy_0 dz_0 = f(\tau).$$

Therefore

$$\Omega_0 = \frac{f(t)}{\{(x-\xi(t))^2 + (y-\eta(t))^2 + (z-\zeta(t))^2\}^{\frac{3}{2}}}, \quad (20)$$

$$\Omega' = -\Omega_0 - \int_{-\infty}^t R f(\tau) \frac{z-\zeta(\tau)-R(t-\tau)}{\{(x-\xi(\tau))^2 + (y-\eta(\tau))^2 + (z-\zeta(\tau)-R(t-\tau))^2\}^{\frac{3}{2}}} d\tau. \quad (21)$$

This is the expression for the magnetic potential due to the induced currents on the negative side of the sheet, *i. e.* on the opposite side to the moving pole; and it is to be observed that  $z$  is taken to be negative on this side.

The quantity  $\Omega''$ , which represents the potential due to the induced currents on the positive side (where  $z$  is positive), is given by

$$\Omega'' = \frac{f(t)}{\{(x-\xi(t))^2 + (y-\eta(t))^2 + (z+\zeta(t))^2\}^{\frac{3}{2}}} - \int_{-\infty}^t R f(\tau) \frac{z+\zeta(\tau)+R(t-\tau)}{\{(x-\xi(\tau))^2 + (y-\eta(\tau))^2 + (z+\zeta(\tau)+R(t-\tau))^2\}^{\frac{3}{2}}} d\tau \quad (22)$$

and the complete expression for the potential due to the induced currents and the moving pole itself is, by (4),

$$\Omega_2 = \Omega_0 + \Omega''.$$

10. The components of magnetic force at  $(x, y, z)$  due to the induced currents alone are respectively

$$-\frac{d\Omega''}{dx}, \quad -\frac{d\Omega''}{dy}, \quad -\frac{d\Omega''}{dz};$$

and the components of the force on the pole itself at any time  $t$  are found by multiplying these expressions by the strength of the pole, *i. e.* by  $f(t)$ , and putting  $x=\xi(t)$ ,  $y=\eta(t)$ ,  $z=\zeta(t)$  after the differentiations have been performed.

In particular, if the pole moves along a straight line perpendicular to the plate, and we take this line as axis of  $z$ , the force on the moving pole itself

$$=f(t) \times \left\{ \frac{f(t)}{\{2\zeta(t)\}^2} - 2R \int_{-\infty}^t \frac{f(\tau) d\tau}{\{\zeta(t) + \zeta(\tau) + R(t-\tau)\}^3} \right\}. \quad (23)$$

The well-known case in which a pole is suddenly generated at the time  $t=0$ , and its strength remains constant and equal to  $m$  after that time, is deduced by making

$$f(t)=0 \quad \text{from } t=-\infty \text{ to } t=0,$$

$$f(t)=m \quad \text{from } t=0 \text{ to } t=+\infty.$$

We therefore have to write  $m$  for  $f(t)$  in the above expressions and to reduce the inferior limit of integration with respect to  $\tau$  from  $-\infty$  to 0.

The advantage of starting with a fixed instead of a moving pole is more evident in the case of a cylindrical or spherical sheet, especially in the latter, since we are thus enabled to use zonal spherical harmonics only and the analysis is consequently much simplified.

XXII. *The Passage of Hydrogen through a Palladium Septum, and the Pressure which it produces.* By WILLIAM RAMSAY, F.R.S.\*

IT has been frequently cited as an argument in favour of attributing the osmotic pressure exercised by a substance in dilute solution on the walls of a vessel permeable to the solvent but not to the dissolved substance, that if a vessel were constructed of palladium, which, as Graham's researches showed, is permeable to hydrogen, but not to many other gases, such a vessel would be subjected on its interior walls to a high pressure if it were filled with an indifferent gas and exposed on its exterior to an atmosphere of hydrogen. The gas confined in the vessel, not being able to escape, would exert the pressure at which it was allowed to enter; while

\* Communicated by the Physical Society: read May 25, 1894.

the interior of the vessel would be a vacuum to hydrogen ; and as its walls are permeable to hydrogen, pressure should rise by passage of hydrogen into the interior, until the pressure of the hydrogen on the interior walls became equal to that on the exterior walls. The effect of this would be to superadd the pressure of the hydrogen to that of the gas originally contained in the vessel ; and if it be supposed that the vessel was originally filled at atmospheric pressure, the entry of hydrogen should increase that pressure by another atmosphere, providing the hydrogen surrounding the exterior walls of the vessel be at atmospheric pressure.

It has been suggested that when pressure is raised by the passage of water into the interior of a cell with semipermeable walls containing a solution, the rise of pressure is due, not to the pressure exercised by the molecules of the dissolved substance, but to that produced by the entering water. Gases present us with an exact analogy. It is idle to inquire what causes the rise of pressure in the interior of such a palladium "cell." The total pressure is due to the hydrogen and to the gas with which the cell was originally filled ; the original pressure has undoubtedly been increased by the entry of hydrogen. But a portion of the pressure—and the effective portion, from the point of view of osmotic pressure—is due to the original gas, whether nitrogen, carbon dioxide, or any gas whatever to which the cell-walls are impervious, and which is not chemically attacked by hydrogen. It is therefore quite correct to ascribe osmotic pressure to the dissolved substance, although it is apparently produced by entry of solvent.

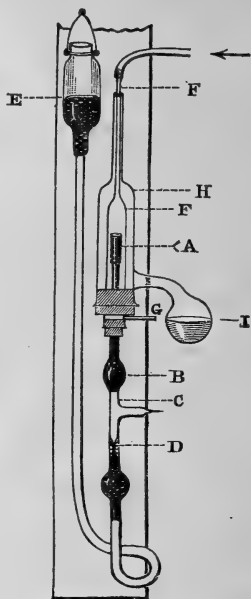
The experiments to be described were made with the object of submitting this entry of hydrogen through the walls of a palladium cell to quantitative study. After considerable progress had been made, a paper by A. Biltz (*Zeitschr. f. phys. Chem.* ix. p. 152) was published, describing lecture-experiments devised to show the ordinary diffusion of gases without a septum, diffusion with a leaky septum of porous earthenware, and also diffusion with a semipermeable septum, permitting the passage of hydrogen, but hindering the passage of other gases. Biltz employed for the last-mentioned purpose an iron tube, and made a few rough quantitative measurements ; but he does not appear to have continued any experiment long enough to obtain a maximum pressure, nor was his apparatus designed with the object of quantitative measurement, but only for the purpose of class demonstration.

*Description of Apparatus.*

The apparatus which was employed is represented in the accompanying woodcut.

AB is a tube of platinum, the top portion of which, at A, is of palladium and closed at its upper end. At B the platinum tube is sealed or cemented on to a glass tube C, with a lateral branch, represented in the figure as drawn off and closed. Somewhat lower down, the tube is sealed to a capillary D, on which graduations are etched. The tube then widens to a bulb, and is finally connected by thick flexible tubing to a reservoir of mercury E.

The palladium tube is surrounded by a glass tube F, also provided with a lateral exit at G, and fitting tightly into a jacket H, which may be heated by boiling the liquid in the bulb I. A gas, passed in at F, would thus surround the palladium tube and escape at G; or if heavier than air, if introduced at G it would escape at F. The palladium cell could be heated to any desired temperature by choosing an appropriate jacketing vapour. The whole apparatus stood in front of a glass mirror-scale, on which the level of the mercury at D and E could be read off. It was possible to read to one tenth of a millimetre, but such accuracy of reading was generally unnecessary.

*Description of an Experiment.*

A clip was placed on the india-rubber tube joining D and E, and the side-tube C, which at this time was open, was connected with a reservoir of some gas, *e. g.* of nitrogen, by means of a three-way tap. The palladium tube was pumped empty, and then filled with dry nitrogen; the operation was repeated ten times, so as to ensure absence of air. The nitrogen was finally allowed to enter the apparatus under slight pressure, and the side-tube C was sealed. The liquid in I was then boiled so as to jacket the tubes F and A, and

the clip on the india-rubber tube was opened. When the temperature had become constant, the reservoir of mercury E was brought approximately to a level with a mark on the capillary tube D, and the capillary tube at C was broken. Gas then escaped through C until the pressure in the tube A became equal to that of the atmosphere. The capillary point was again sealed. An accurate reading was then taken, the mercury reservoir being placed so that an exact volume of gas was contained in the palladium cell under a known pressure.

Hydrogen carefully purified by washing with potassium permanganate, silver nitrate, and caustic potash, and dried by passage through sulphuric acid and over phosphorus pentoxide, was then passed in through the tube F, escaping at G. Pressure rapidly rose in the interior of the apparatus, and was measured by raising the mercury reservoir. When it had attained its maximum a reading was taken, the position of the mercury in the capillary stem being so adjusted that the capacity of the cell was accurately the same as at the commencement of the experiments. The difference between the initial and final pressure is due to entry of hydrogen.

The success of such experiments depends on the condition of the palladium. After having been used once or twice the interior of the palladium tube became coated with mercury, even although the level of mercury (which was cold) lay far below the palladium top. It appears that palladium absorbs mercury-vapour with avidity, thus rendering the palladium cell a partial vacuum to mercury-vapour. Vapour rises from the cold mercury to restore pressure, and is again absorbed. It was therefore necessary to heat the palladium tube after each experiment in order to expel mercury. This had the effect of oxidizing the palladium and of covering it with a brownish-black film. To remove the oxide, the tube was made the negative pole of a battery, and dilute sulphuric acid was electrolysed, both on the inside and outside of the palladium tube. It was then dried at a low temperature; the external surface was polished with a little dry emery; the tube was cemented into its place, and was ready for a fresh experiment. Without such precautions the passage of hydrogen is very slow and incomplete. It should be mentioned that before commencing an experiment it was necessary to jacket the palladium tube at  $220^{\circ}$  and to pass a current of air over it for some time. In this way the combined hydrogen was removed; hydrogen escaped from the exterior of the tube and was replaced by air or some other gas in the interior.

*Account of Experiments.*

The experiments admit of classification under five heads:—

1. Experiments with the tube filled with air.
2. Experiments with the tube filled with nitrogen.
3. Experiments in which the hydrogen passed over the exterior of the tube was diluted with nitrogen or other gases, when it exercised only a partial pressure on the exterior walls of the tube.
4. Experiments in which the palladium tube was filled with other gases.

5. Experiments with a nickel tube and carbon monoxide.

*Experiment 1.*—The tube was filled with air and jacketed with bromonaphthalene, boiling at about  $280^{\circ}$ . The barometric pressure during the experiment was constant at 743.1 millim. On passing hydrogen for three hours the pressure in the palladium cell had become constant; the rise of pressure was 573 millim.

Water appeared on the surface of the mercury in the capillary tube, showing that the hydrogen had combined with the oxygen of the air. The rise of pressure measured should therefore have been that of the nitrogen remaining in the cell, viz. 585 millim.

It may be concluded, then, that hydrogen combines with oxygen in presence of palladium at  $280^{\circ}$ , and that the residual nitrogen exerts nearly its partial pressure; or, as will be afterwards shown to be a more correct statement, the nitrogen exerts its full partial pressure, and the hydrogen in the interior exerts a large fraction of the pressure of the external hydrogen.

*Experiment 2.*—The tube was filled with pure dry nitrogen, and exposed to hydrogen, as before, at the same temperature. The pressure, after it had become fairly steady, was 703.2 millim. in excess of that of the atmosphere (748.1 millim.). The hydrogen was next removed by passing a current of air over the exterior of the tube, and the pressure was again raised by a current of hydrogen. After about three-quarters of an hour the pressure was 699.8 millim. in excess of that of the atmosphere, a quarter of an hour later it was 721.1 millim., and in another quarter of an hour it had risen to 733.0 millim. It appeared then to be stationary. The barometric pressure was still 748.1 millim.; it therefore appears that the pressures of the hydrogen on the exterior and interior of the palladium tube were nearly equal.

It was noticed during these experiments that when the gas was changed the pressure invariably fell a little on admitting hydrogen and rose a little on admitting oxygen; the direction

of the pressure then changed, and the usual rise with hydrogen and fall with air occurred. I think that this is to be attributed to the fact that the palladium vessel increases its capacity suddenly on exposure to hydrogen, and decreases it on exposure to air after having been exposed to hydrogen. But the total change of volume is a very minute one; it is noticeable only by the rise or fall of the mercury in the capillary tube to the amount of one or two millimetres; and the total change of volume is certainly less than 0.1 per cent. of the capacity of the vessel.

*Experiments 3, 4, and 5.*—The next three experiments gave readings much lower than those previously obtained. The barometric reading was 748.6 millim. The rise in experiment 3 was 650.3 millim.; in experiment 4, 654.2 millim.; and in experiment 5, 657.8 millim.

This led me to suspect that the palladium tube had undergone alteration. It was therefore disconnected and cleaned as before described. It was finally filled with nitrogen.

*Experiments 6, 7, 8, 9, and 10.*—The barometric pressure was 770.2 millim. The final pressure in experiment 6 was 698.5; in 7, 692.1; in 8, the barometric pressure being 768.8 millim., the final pressure was 686.4 millim. In experiment 9, with a barometer-reading of 762.2 millim., the reading was 692.4 millim.; and in 10, the barometer-reading being 759.2, the pressure was 688.4 millim.

To summarize these results it is necessary to compare the pressure of the internal hydrogen with that of the external hydrogen. The following table gives their ratios:—

Experiment.	(1)	(2)	(3)	(4)	(5)
Ratio . . . .	0.9400	0.9798	0.8687	0.8739	0.8780
Experiment.	(6)	(7)	(8)	(9)	(10)
Ratio . . . .	0.9069	0.8986	0.8928	0.9084	0.9067

These results do not exhibit any great degree of constancy, but I am sure that their difference depends largely, if not wholly, on the state of the surface of the palladium. The mean result is 0.9053, a number closely approximating to the last five determinations. This would lead to the conclusion that the pressure of the internal hydrogen rises to rather more than  $\frac{9}{10}$  of the pressure of the external hydrogen at 280°.

*Experiment 11.*—The temperature was now kept at the boiling-point of quinoline (about 237°). The passage of hydrogen through palladium is so slow at this temperature that

patience failed me to make more than one determination. It was begun on May 4th. On May 10th pressure was still rising, but very slowly. On May 11th it had reached 501·7 millim.; on the 13th it was 525·2 millim., and on the 14th 531·2 millim. Taking the figure actually read, the fractional pressure (barometer = 766·3 millim.) was 0·6932. Judging from this experiment, the pressure would appear to depend on the temperature of the palladium and of the hydrogen. Still, it is possible that had the experiment been carried on sufficiently far, the pressure might have risen much higher.

*Experiment 12.*—The next set of experiments was made at a higher temperature—that of the boiling-point of dibenzylketone (335°). The pressure registered at a barometric height of 758·7 millim. was 681·6 millim. The ratio is 0·8984, practically identical with that obtained at the boiling-point of bromonaphthalene.

*Experiments 13, 14, and 15.*—The hydrogen in these experiments was mixed with 50 per cent. of nitrogen, so that the exterior of the palladium tube was exposed to a partial pressure of hydrogen. The first of this set gave a pressure of hydrogen of 367·9 millim., the barometer standing at 770·9 millim.; the second, 352·9 millim., barometer at 771·8 millim.; and the third 362·7 millim. at the same pressure.

*Experiment 16* was made with a mixture of one volume of hydrogen to three of nitrogen; the read pressure was 176·7 millim., the barometric height being 756·5 millim.

The ratios are :—

Experiment.	13	14	15	
Ratio . . . .	0·4771	0·4573	0·4700.	Mean 0·4681.

Experiment 16 : Ratio 0·2336.

Multiplying the first mean ratio by 2, and the second by 4, the products are comparable with that from pure hydrogen. The figures are :—

Pure hydrogen . . . . .	0·9053
Hydrogen + 50 p. c. nitrogen . . .	0·9362
Hydrogen + 75 p. c. nitrogen . . .	0·9344

The pressure, as might have been anticipated, is proportional to the partial pressure of the external hydrogen.

It is obviously possible to test the percentage of hydrogen in coal-gas by this means, provided the other constituents of coal-gas are unable to pass through palladium. An experiment with marsh-gas showed that it is not capable of permeating palladium; and the vapour of ether is also unable to pass.



*Experiments 17 and 18.*—At  $280^{\circ}$  the pressures with a sample of London coal-gas were 364.4 millim., at a barometric pressure of 760.4 millim.; and 361.8 millim. at a barometric pressure of 761.5 millim. The ratios are 0.4792 and 0.4751 respectively. Supposing the highest attainable ratio to be 0.9053, as deduced from the ten experiments with pure hydrogen, the percentage of hydrogen is easily found by the ratios  $(0.4792 \times 100)/0.9053$ , and  $(0.4751 \times 100)/0.9053$ . The numbers are 52.94 and 52.49 per cent. respectively. It would be possible thus to have a continuous register of the percentage amount of hydrogen in coal-gas, provided the palladium did not alter its state. As it is, I am afraid that the apparatus will not retain its activity for a sufficiently long time. It should also be remarked that it is necessary to wash the coal-gas with a solution of potassium permanganate, in order to free it from sulphur compounds. If this precaution is not taken, the palladium becomes coated with a layer of sulphide, and it ceases to be permeable to hydrogen.

Experiments were next made in which the palladium tube contained various gases.

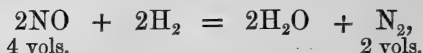
*Experiment 19.*—The tube contained carbon dioxide. On exposing it to hydrogen at  $280^{\circ}$  the pressure rose with great rapidity—much more rapidly than had previously been observed. The rise ceased at 735 millim., the barometric pressure being 764.0. The quotient is 0.9621, a higher number than any yet obtained.

*Experiment 20.*—Carbon monoxide was in the interior; the pressure rose rapidly on admission of hydrogen to 734.5 millim., the barometer reading 769.5. The quotient is 0.9545, also a very high number. In both of these experiments the fall on passing air over the exterior of the tube was much slower than the rise with hydrogen. The end point was difficult to note, for the last change of pressure was very slow. It may be that the exterior surface of the palladium being exposed to hydrogen alone, little difficulty was experienced in molecules entering; but that on reversing the action, the contact of hydrogen with the interior walls was interfered with by the indifferent gas present. The same phenomenon had previously been noticed, but in a minor degree. It is noteworthy that no trace of water was formed in either case. Hydrogenized palladium is without action on carbon monoxide or dioxide at  $280^{\circ}$ .

*Experiment 21.*—The tube was filled with cyanogen. The total pressure was 741 millim., the barometer standing at 764.5 millim. The quotient is 0.9693, a very high number. On substituting air, the cyanogen exerted finally a pressure of

740 millim. This would appear to indicate that palladium is quite impermeable to cyanogen, and is not attacked by it at 280°.

*Experiment 22.*—Nitric oxide was introduced into the tube, at a barometric pressure (corrected) of 765 millim. On passing hydrogen the pressure rose 368 millim.; the total pressure of the gases in the tube was  $368 + 763 = 1131$  millim., the barometric height being 763 millim. The increase of pressure was therefore  $1131 - 765 = 366$  millim. Supposing that the nitric oxide had reacted with the hydrogen, forming nitrogen and water, thus:—



the pressure of the nitric oxide would have been halved, and would have amounted to  $765/2 = 382.5$  millim. But it is to be supposed that the resulting water would have exerted its usual vapour-pressure; and as its temperature was 22°, the pressure of the water-vapour would be 18.5 millim.

We have thus:—

					millim.
Pressure of $\text{H}_2 + \text{N}_2 + \text{H}_2\text{O}$ vapour .	368	+	763		= 1131
Pressure of $\text{N}_2 + \text{H}_2\text{O}$ vapour . .	382.5	+	18.5		= 401

Hence pressure of hydrogen alone = 730

and the quotient  $730/765 = 0.9543$ , a number almost identical with those previously obtained.

*Experiment 23.*—A similar experiment was made with nitrous oxide. Here, too, reduction occurs at 280°; but the volume of the residual nitrogen is equal to that of the nitrous oxide.

The initial pressure of the nitrous oxide was 772 millim. After passing hydrogen, the total pressure was 1489.5 millim. The difference, 717.5 millim., is to be ascribed to hydrogen and water-vapour. The barometer stood at 761 millim. Deducting 18.5 millim., the pressure of water-vapour at 22°, the pressure of the hydrogen alone is 699 millim. And the quotient  $699.0/761 = 0.9186$ .

The hydrogen was then removed by a current of air on the external surface of the palladium. The pressure of the nitrogen was then 780.5 millim. Again restoring hydrogen on the exterior, the pressure rose to 727.5 millim., the barometric pressure being 761 millim. The pressure ascribable to hydrogen and water-vapour is thus 708 millim.; subtracting the pressure of water-vapour, 22.5 millim., the remainder, 685.5 millim., is due to hydrogen. The quotient is 0.9008. Here again a reasonable correspondence is found.

It is evident that in all cases the pressure of the hydrogen in the interior of the palladium tube is lower than the barometric pressure, *i. e.* lower than the pressure of the hydrogen on the exterior. It will be convenient here to tabulate the ratios found :—

a. Mean ratio from hydrogen and nitrogen at 280° .	0.9053
b. Ratio at 335° . . . . .	0.8984
c. Ratio with 50 per cent. of hydrogen at 335° . .	0.9362
d. Ratio with 25 per cent. of hydrogen at 335° . .	0.9344
e. Ratio from hydrogen and carbon dioxide at 280° .	0.9621
f. Ratio from hydrogen and carbon monoxide at 280° .	0.9545
g. Ratio from hydrogen and cyanogen at 280° . .	0.9693

I omit the two last determinations, as uncertainty was introduced owing to the presence of water-vapour.

On reviewing these results, it would appear that the ratio is not altered by rise of temperature above 280°. The same number was obtained at 280° and at 335°. But at a lower temperature the ratio is much smaller, if, indeed, the end-point was really reached. Dilution of the hydrogen appears to raise the ratio ; and the presence of carbon dioxide, carbon monoxide, or cyanogen in the interior of the palladium tube appears to be favourable to the passage of hydrogen.

To what are these results to be ascribed ?

Troost and Hautefeuille have determined the pressures of dissociation of the definite hydride of palladium,  $\text{Pd}_2\text{H}$  (*Compt. rend.* lxxviii. p. 686). At 130° the pressure is nearly equal to that of the atmosphere, it is 624 millim.; while at 140° the pressure is 812 millim. It rises rapidly with temperature, and at the highest temperature given, 170°, it amounts to the large number 1840 millim. It is impossible to believe, then, that any hydride of palladium should exist even at the lowest of the temperatures employed, 223°. Yet palladium becomes quickly permeable to hydrogen only at a higher temperature.

Two questions require answer :—(1) Why is palladium permeable to hydrogen ? and (2) Why is the pressure of the internal hydrogen always less than that of the external hydrogen ?

(1) It is hardly probable that the palladium acts simply as a filter, allowing small molecules of hydrogen to pass while blocking the passage of larger molecules of other gases. Graham, however, appears to regard this as in some measure the cause of the passage. His words are :—“ Such phenomena of gaseous penetration appear to suggest a progression in the degree of porosity. There appear to be (1) pores through which gases pass under pressure or by capillary transpiration, as in

dry wood and many minerals ; (2) pores through which gases do not pass under pressure, but pass by their proper molecular movement of diffusion as in artificial graphite ; and (3) pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite."

It is noteworthy that Graham considers that gases are liquefied in the pores of metals. But in the experiments here described this can hardly be the case. For at  $270^{\circ}$  and at higher temperatures hydrides of palladium do not exist, as is conclusively shown by Troost and Hautefeuille ; just as water does not exist in superheated steam. And yet it is at these temperatures that palladium is permeable to hydrogen, and not at temperatures at which hydride of palladium is stable.

There are several facts which must be borne in mind in seeking for an interpretation for the phenomenon of the passage of hydrogen through palladium.

First. The hydrogen in the act of passing is a reducing agent, as shown by its behaviour towards the oxides of nitrogen. At such temperatures as were here employed, hydrogen is without action on the lower oxides of nitrogen.

Second. Bellati and Lussano have shown (*Atti R. Ist. Ven.* i. series vii. p. 1173) that hydrogen "diffuses" through an iron plate which is used as a negative electrode on electrolysing dilute sulphuric acid. Their observation has been confirmed and amplified by Shields (*Chem. News*, lxx. p. 195). Shields has shown that neither lead nor platinum nor palladium allow hydrogen to pass under similar circumstances, and experiments made by myself show that nickel does not allow carbon monoxide to pass at temperatures at which that compound is stable.

Third. Iron and platinum, as shown by Deville and Debray (*Compt. rend.* lvii. p. 965), are permeable at a red heat to hydrogen.

I think these considerations prove that it is necessary to add a fourth class to the three classes suggested by Graham. Graham's first class involves actual holes, that is, passages large in comparison with the molecular diameter ; his second implies pores small compared with molecular diameter, but still greatly exceeding that diameter ; his third class would be termed "solid solution" in the present state of our knowledge, *i. e.* when coal-gas passes through india-rubber, the latter dissolves the gas on the side exposed to it, while the gas evaporates from the other side, so as to render the pressure of the dissolved gas equal on both sides of the membrane.

The case is precisely analogous to the passage of water through a semi-permeable diaphragm. But, in order that hydrogen may pass through iron, it must be in the state in which it is liberated by an electric current, or it must be hot. That hydrogen will not pass through palladium at the ordinary temperature appears to show that the compound of palladium and hydrogen has practically no dissociation pressure at ordinary temperature; otherwise the hydrogen would pass by solution, in the same manner as coal-gas passes through india-rubber, or water through a semi-permeable diaphragm. That it will not pass, even when liberated by an electric current on one side of the palladium membrane, shows that it at once enters into combination with the palladium, and is no longer *in statu nascendi*, to use a generally understood expression which is independent of theory. But that it passes through hot palladium appears to show that it is then in a state analogous to that of electrically liberated hydrogen.

It is known that electrified bodies are discharged if a flame burns in their vicinity. This may be attributed to the liberation of atomic oxygen in a kind of Grotthus chain. For it may be imagined that when a molecule of oxygen encounters the oxidizable matter of a flame, it is dissociated: while one atom serves to oxidize the carbon, the other exchanges with a neighbouring molecule, and a succession of exchanges occur till the atomic oxygen near the electrified body receives or communicates a charge, and restores the potential of the charged body to that of surrounding objects.

To ascertain whether a flame of oxygen burning in hydrogen would similarly cause the hydrogen to assume the atomic state, a piece of apparatus was contrived in which such a flame burned in close proximity to a very thin iron plate, on the other side of which a Torricellian vacuum was maintained. No hydrogen passed through the plate: hence either the hydrogen was not atomically transferred, as oxygen is supposed to be under similar circumstances, or such atoms were unable to pass through the plate as they would have done if liberated electrically. It must be noticed, however, that it is conceivable that the double atom of hydrogen which we term a molecule may have united directly with the oxygen, without separating into its two components. The result of this experiment is therefore inconclusive.

It appears to me necessary to suppose that at a temperature far above that at which hydride of palladium is capable of existence, the palladium has still the power of so attracting the hydrogen that the molecule is split. This necessarily implies a gain of energy, so far as the splitting of the

hydrogen molecule is concerned, for any energy lost by the temporary and transient union of hydrogen and palladium is at once gained during its escape on the other side of the partition. But the hydrogen in expanding, which it does on passing through the partition, loses energy, and hence, on the whole, energy will probably be lost during the process. It is to such theories, I think, that we must look to explain the passage of hydrogen through a palladium diaphragm.

(2) In answering the question why the pressure raised by the entering hydrogen is never equal to that of the atmosphere, I think it must be admitted that the gas contained in the palladium vessel is not without influence on the passage of the hydrogen. A diminution of the pressure of the external hydrogen by the addition of nitrogen considerably increases the partial pressure of the internal hydrogen. Here the action of external nitrogen apparently neutralizes partially the effect of the internal nitrogen, and more hydrogen penetrates the metallic diaphragm. With gases other than nitrogen in the interior, the pressure of the hydrogen becomes more nearly equal to that on the exterior. The constancy of the results, however, proves that the deficiency is not due to experimental error.

This whole subject is full of difficulty. Experiments are in progress on the absorption of gases by platinum, and on the passage of gases through other metallic diaphragms, which may ultimately render an explanation possible. But I have thought it desirable to place these experiments on record, incomplete as they are, rather than wait for a complete solution to the problem.

I cannot conclude without acknowledging the able manner in which my late assistant, Mr. Percy Williams, has aided me in carrying out these experiments.

### XXIII. *Note on the Rigidity of the Earth.*

*By M. P. RUDSKI, Odessa\*.*

PROF. NEWCOMB† has estimated the Rigidity of the Earth from the observed 427 days'‡ period of the Variations of Latitude, and found it to be somewhat greater than that of steel. His estimation being a rough one, I have undertaken a more precise calculation with the help of the formulas of Thomson and Tait.

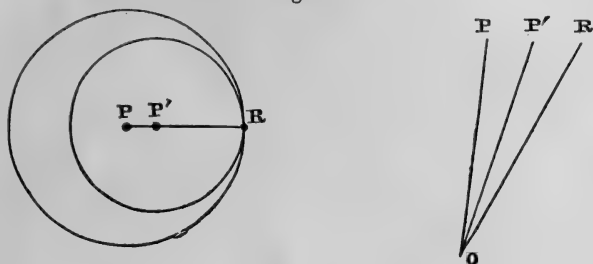
\* Communicated by the Author.

† Monthly Notices Astron. Soc. 1892, pp. 336-341.

‡ The recent investigations of the astronomers of Poulkova confirm also this period.

Prof. Newcomb begins with the remark that the condition for the possibility of the 427 days' period is, that the pole of the principal axis shall be at a distance from the North Pole [that is from the point which would be the pole of rotation and inertia if the perturbation did not exist] equal to  $\frac{2}{3}$  of the distance between the pole of rotation and the North Pole. (See fig. 1.) Thus the pole of rotation R revolves in nearly

Fig. 1.



P, the North Pole.  
P', pole of the principal axis.  
R, pole of rotation.  
O, centre of inertia.

305 days about the pole of inertia P', but this latter and also R revolve about the North Pole in 427 days. The little circle is rolling on the greater.

The precise statement of the problem is the following :—

The equations of motion relatively to axes revolving with angular velocities  $p, q, r$  are of course :

$$\rho \left[ \frac{d^2 x}{dt^2} - 2r \frac{dy}{dt} + 2q \frac{dz}{dt} - x(q^2 + r^2) + y \left( pq - \frac{dr}{dt} \right) + z \left( \frac{dq}{dt} + pr \right) \right] = X.$$

. . . . .

Suppose that the body is elastic, that  $x_0, y_0, z_0$  are the coordinates of particles belonging to their *undisturbed* positions, suppose that  $\xi, \eta, \zeta$  are the displacements, suppose that the revolving axes are fixed relatively to the coordinates  $x_0, y_0, z_0$ , then  $x_0, y_0, z_0$  are constants, and as

$$\begin{aligned} x &= x_0 + \xi, \\ y &= y_0 + \eta, \\ z &= z_0 + \zeta, \end{aligned}$$

$\frac{d^2 x}{dt^2}$  reduces to  $\frac{d^2 \xi}{dt^2}$ , and so on.

Further, neglecting  $\xi, \eta, \zeta$  in comparison with  $x_0, y_0, z_0$ ,





where  $n$  is the coefficient of rigidity,  
 $\frac{m}{V}$  is the potential of attraction, incompressibility,

$$\phi = \frac{\rho\omega^2}{2} [x^2(b^2 + c^2) + y^2(a^2 + c^2) + z^2(a^2 + b^2) - 2xy ab - 2xz ac - 2yz bc],$$

$\rho$  means the mean density,

$$\delta = \frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz},$$

$\nabla^2$  is the known Laplacian symbol.

$V$  may now be divided in two parts, the first corresponding to the potential of the unstrained body, the other containing all the terms which arise in consequence of the deformation : so we may write

$$V = V_1 + V_2.$$

On the other hand, with the help of the formula

$$a^2 + b^2 + c^2 = 1,$$

we may write for

$$\begin{array}{ll} b^2 + c^2, & 1 - a^2, \\ a^2 + c^2, & 1 - b^2, \\ a^2 + b^2, & 1 - c^2. \end{array}$$

Now if the  $Z$  axis of coordinates coincides with the *polar* axis of the earth corresponding to the unstrained state, the potential

$$V_1 + \rho\omega^2(x^2 + y^2)$$

exerts no deformation, so that in equations (I.)  $V$  reduces to  $V_2$  and  $\phi$  becomes

$$\phi = -\frac{\rho\omega^2}{2} [x^2a^2 + y^2b^2 + z^2(c^2 - 1) + 2xy ab + 2xz ac + 2yz bc].$$

We see that  $\phi$  is a solid harmonic of the second degree.

But the disturbing potential is

$$V_2 + \phi.$$

To find it, we proceed after the method of Prof. Darwin\*, and obtain readily

$$W_2 = V_2 + \phi = \frac{19n}{19n + 2g\rho R} \cdot \phi. \quad \text{. . . (II.)}$$

\* "On Bodily Tides," Phil. Trans. for 1879, p. 9. The calculus is "literatim" the same.

Here we have made the supposition that the body is *incompressible*. [R means the mean radius of the Earth.]

We must now calculate the products and the moments of inertia about old axes after deformation.

As this calculation implies the knowledge of the displacements, we shall take the expressions of the displacements given by Thomson and Tait\* for the case of a sphere

$$\xi = \frac{1}{38n} \left[ (8R^2 - 5r^2) \frac{dW_2}{dx} + yxW_2 \right] \quad \dots \quad (\text{III.})$$

$$\begin{matrix} \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{matrix}$$

Before calculating the products of inertia we remark that the deformation is evidently symmetrical with respect to the plane passing through the axis of  $z$  and the axis of rotation.

Hence, taking this plane for the plane XZ †, we obtain first, if D, E, F are the products of inertia,

$$D = F = 0;$$

secondly,

$$\phi = \frac{\rho \omega^2}{2} [a^2(z^2 - x^2) - 2xzac] \quad \dots \quad (\text{IV.})$$

Now, the calculation of

$$E = \Sigma m(x + \xi)(z + \zeta),$$

with the help of the formulas II., III., and IV. is very easy, and gives

$$E = -a \cdot c \cdot \frac{\rho}{19n + 2g\rho R} \cdot MR^2 \cdot u^2,$$

where M is the mass of the earth,

$u$  the equatorial velocity ( $u = \omega R$ ).

We shall also need the difference C - A. This difference, being very little changed by the deformation, may be directly calculated from the known values

$$C = 0.3321 \cdot MR^2,$$

$$A = 0.3310 \cdot MR^2,$$

so that

$$C - A = 0.0011 MR^2.$$

\* Treat. on Nat. Phil. arts. 837, 838.

† In this manner we introduce coordinates moving respectively to the body, but evidently it does not change anything in the results.

Now, by a known theorem, if

$$D = F = 0,$$

the moments of inertia about the new principal axes are the roots of the equation

$$(H-A)x^2 + (H-B)y^2 + (H-C)z^2 + 2E\,xz = 0, \quad (V.)$$

where A, B, C are the given moments about the old axes.

In the present case we may put

$$A = B.$$

Now, if the angle between the axis of the new greatest moment of inertia and the axis of  $z$  is  $\theta$ , then by the transformation

$$x = x_1 \cos \theta + z_1 \sin \theta,$$

$$z = -x_1 \sin \theta + z_1 \cos \theta,$$

we may easily find the angle  $\theta$  from the formula V. We obtain

$$\tan 2\theta = -\frac{2E}{C-A}. \quad \dots \dots (VI.)$$

But by definition the angle  $\theta$  ( $\angle POP'$ ) is equal to  $\frac{1}{2}$  of the angle POR, and

$$c = \cos (POR)$$

$$a = \sin (POR)$$

As the angles POR and POP' are very small, their cosines are nearly equal to unity, and their sines are nearly equal to the arcs; but the arc POR is equal to  $\frac{1}{2}$  of the arc POP' [the arc  $\theta$ ]. Hence, neglecting small quantities of second order, we obtain from the formula VI.

$$\frac{4}{7} = \frac{2 \cdot \rho}{19n + 2g\rho R} \cdot \frac{u^2}{0.0011} \cdot \dots \dots (VII.)$$

But Prof. Newcomb thinks that one fourth of the angle POP' may be attributed to the influence of the Ocean. Further, as the product of inertia E standing in the numerator of the right-hand member of VI. depends principally on the deformation of superficial layers, and for that reason the mean density in E must be smaller than the mean density of the Earth—we must multiply the right-hand member of VII. by a factor smaller than unity. We take, with Prof. Newcomb, the mean effective density to be 0.6 of that of steel, *i. e.* 4.68, and multiply the right-hand member of VII.

with  $\frac{4.68}{5.5}$ . It is to be remarked that by the meaning of

mean densities  $\rho$  contained in VII., they are all to be taken inferior to the mean density of the Earth. Now the formula VII. changes to

$$\frac{3}{7} = \frac{2 \times 4.68 \times u^2}{5.5 \times 0.0011 \left[ 19 \frac{n}{\rho} + 2gR \right]}.$$

$u = 46,500$  centim. per sec.,

$R = 637,000,000$  centim.,

$g = 981$  centim. per sec.

$\rho = 4.68$  [Prof. Newcomb's effective mean density].

With these data,

$$n = 1615 \times 10^9.$$

This coefficient of rigidity is nearly twice as great as the coefficient of rigidity of steel after Everett [ $819 \times 10^9$ ]. By certain combinations of the chosen effective mean densities in the numerator and denominator of VII., also putting again  $\frac{4}{7}$  instead of  $\frac{3}{7}$  in the left-hand member, we may render the coefficient of rigidity smaller. But it remains much greater than the coefficient for steel.

The proof of the rigidity of the Earth from the tidal phenomena was subject to certain doubts\*, but now it is strongly supported by the test of the phenomenon of Variation of Latitudes.

M. Gylden† has presented some objections to the views of Lord Kelvin and Prof. Newcomb. Without discussing his paper, we remark only that we can interpret his analysis as corresponding to the case of an *absolutely* rigid earth with certain fluid or generally mobile parts. Of course he has found that these mobile parts must be greater than the Oceans. We have taken the Earth as incompressible. It is known that this assumption has a very little influence on the final results. In a quite similar case, that of the tidal problem, Mr. Love‡ has obtained nearly the same results on the hypothesis of compressibility [ $m = 2n$ ] as on the hypothesis of perfect incompressibility [ $m = \infty$ ].

\* See Prof. Darwin's paper, Proc. Roy. Soc. London, Nov. 1886.

† *Compt. rendus*, vol. cxvi. (1893), pp. 476-479.

‡ Transactions Cambr. Phil. Soc. vol. xv. pp. 107-118.

XXIV. *On the Electrification of Air.* By Lord KELVIN,  
P.R.S., and MAGNUS MACLEAN, M.A., F.R.S.E.\*

§ 1. **T**HAT air can be electrified either positively or negatively is obvious from the fact that an isolated spherule of pure water, electrified either positively or negatively, can be wholly evaporated in air†. Thirty-four years ago it was pointed out by one of us‡ as probable that, in ordinary natural atmospheric conditions, the air for some considerable height above the earth's surface is electrified§

\* Communicated by the Authors; having been read before the Royal Society, May 31, 1894.

† This demonstrates an affirmative answer to the question, Can a molecule of a gas be charged with electricity? (J. J. Thomson, 'Recent Researches in Electricity and Magnetism,' § 36, p. 53), and shows that the experiments referred to as pointing to the opposite conclusion are to be explained otherwise.

Since this was written we find, in the 'Electrical Review' of May 18, on page 571, in a lecture by Elihu Thomson, the following:—"It is known that as we leave the surface of the earth and rise in the air there is an increase of positive potential with respect to the ground. . . . It is not clearly proven that a pure gas, rarefied or not, can receive and convey a charge. If we imagine a charged drop of water suspended in air and evaporating, it follows that, unless the charge be carried off in the vapour, the potential of the drop would rise steadily as its surface diminished, and would become infinite as the drop disappeared, unless the charge were dissipated before the complete drying up of the drop by dispersion of the drop itself, or conveyance of electricity by its vapour. The charge would certainly require to pass somewhere, and might leave the air and vapour charged."

It is quite clear that "must" ought to be substituted for "might" in this last line. Thus the vagueness and doubts expressed in the first part of the quoted statement are annulled by the last three sentences of it.

‡ "Even in fair weather the intensity of the electric force in the air near the earth's surface is perpetually fluctuating. The speaker had often observed it, especially during calms or very light breezes from the east, varying from 40 Daniell's elements per foot to three or four times that amount during a few minutes, and returning again as rapidly to the lower amount. More frequently he had observed variations from about 30 to about 40, and back again, recurring in uncertain periods of perhaps about two minutes. These gradual variations cannot but be produced by electrified masses of air or cloud, floating by the locality of observation."—Lord Kelvin's 'Electrostatics and Magnetism,' art. xvi. § 282.

§ "The out-of-doors air potential, as tested by a portable electrometer in an open place, or even by a water-dropping nozzle outside, two or three feet from the walls of the lecture-room, was generally on these occasions positive, and the earth's surface itself therefore, of course, negative—the common fair-weather condition—which I am forced to conclude is due to a paramount influence of positive electricity in higher regions of the air, notwithstanding the negative electricity of the air in the lower

and that the incessant variations of electrostatic force which he had observed, minute after minute, during calms and light winds, and often under a cloudless sky, were due to motions of large quantities of positively or negatively electrified air in the immediate neighbourhood of the place of observation.

§ 2. It was proved\* by observations in the Old College of Glasgow University that the air was in general negatively electrified, not only indoors, within the old lecture-room† of Natural Philosophy, but also in the out-of-doors space of the College Court, open to the sky though closed around with high buildings, and between it and the top of the College Tower. The Old College was in a somewhat low situation, surrounded by a densely crowded part of a great city. In the new University buildings, crowning a hill on the western boundary of Glasgow, similar phenomena, though with less general prevalence of negative electricity in the air, have been observed, both indoors, in the large Bute Hall, and in many other smaller rooms, and out-of-doors, in the court, which is somewhat similar to the courts of the Old College, but much larger. It is possible that the negative electricity found thirty years ago in the air of the Old College may have been due to its situation, surrounded by houses with their fires, and smoking factory-chimneys. In the New College much of the prevalence of negative electricity in air within doors has, however, been found to be due to electrification by the burning lamp‡ used with the quadrant-electrometer; and more recent observations, with electrification by flame absolutely excluded, throw doubt on the old conclusion, that both in town and country negative electrification is the prevailing condition of natural atmospheric air in the lower regions of the atmosphere.

§ 3. The electric ventilation found in the Old College, and described in § 299 of 'Electrostatics and Magnetism,' according to which air drawn through a chink, less than  $\frac{1}{2}$ -inch wide, of a slightly open window or door, into a large room

stratum near the earth's surface. On the two or three occasions when the in-door atmospheric electricity was found positive, and therefore the surface of the floor-walls and ceiling negative, the potential outside was certainly positive, and the earth's surface out-of-doors negative, as usual in fine weather."—*Ibid.* § 300.

\* *Ibid.* Q. 2, § 283.

† *Ibid.* §§ 296-300.

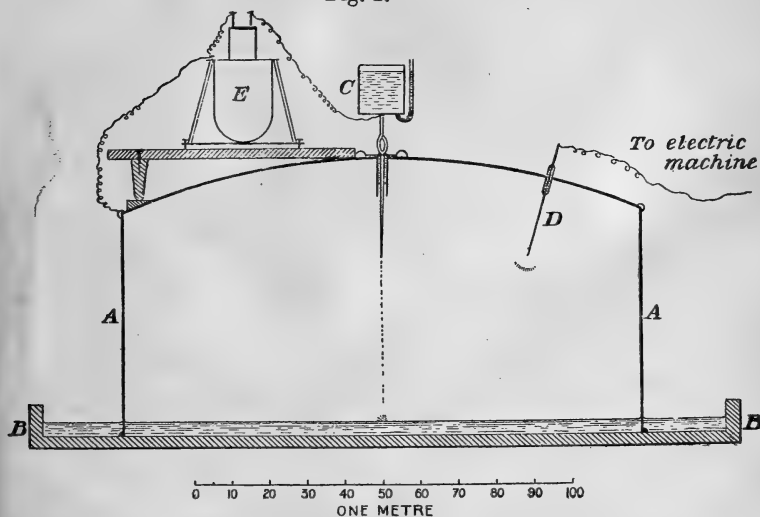
‡ "Electrification of Air by Combustion," Magnus Maclean, M.A., F.R.S.E., and Makita Goto, Philosophical Society of Glasgow, Nov. 20, 1889; "Electrification of Air by Water-Jet," Magnus Maclean, M.A., F.R.S.E., and Makita Goto, 'Philosophical Magazine,' August 1890.

showed the electrification which it had on the other side of the chink, whether that was the natural electrification of the open air, or positive or negative electrification produced by aid of a spirit-lamp and electric machine in an adjoining room, has been tried again in the New College with quite corresponding results. It has also been extended to the drawing in of electrified air through a tube to the enclosure represented in fig. 1 of the present paper; with the result that the water-dropping test indicated in the sketch amply sufficed to show the electrification, and verify that it was always the same as that of the air outside. When the tube was filled with loosely packed cotton-wool the electrification of the entering air was so nearly annulled as to be insensible to the test.

§ 4. The object proposed for the experiments described in the present communication was to find if a small unchanged portion of air could be electrified sufficiently to show its electrification by ordinary tests, and could keep its electrification for any considerable time; and to test whether or not dust in the air is essential to whatever of electrification might be observed in such circumstances, or is much concerned in it.

§ 5. The arrangement for the experiments is shown in the diagram (fig. 1). AA is a large sheet-iron vat inverted on

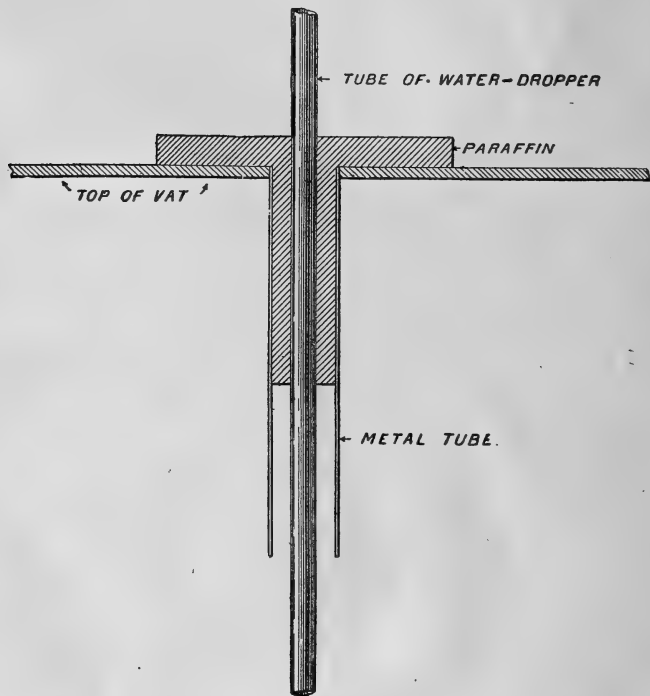
Fig. 1.



a large wooden tray BB, lined with lead. By filling the tray with water the air is confined in the vat. There are two holes in the top of the vat: one for the water-dropper C, and

and one for the charging wire D. Both the water-dropper and the charging wire, ending with a pin-point as sharp as possible, are insulated by solid paraffin, which is surrounded by a metal tube, as shown in half size in fig. 2. To start

Fig. 2.



with they were supported by pieces of vulcanite embedded in paraffin. But it was found that after the lapse of some days (possibly on account of ozone generated by the incessant brush-discharges), the insulation had utterly failed in both of them. The vulcanite pieces were then taken out, and solid paraffin, with the metal guard-tube round it to screen it from electrically influencing the water-dropper, was substituted. This has proved quite satisfactory: the water-dropper, with the flow of water stopped, holds a positive or a negative charge for hours.

§ 6. A quadrant-electrometer E (described in 'Electrostatics and Magnetism,' §§ 346-353) was set up on the top of the vat near the water-dropper, as shown in fig. 1. It was used with lamp and semi-transparent scale to indicate the



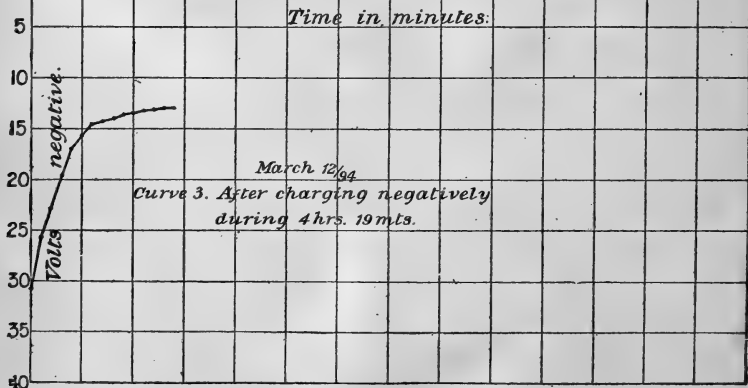
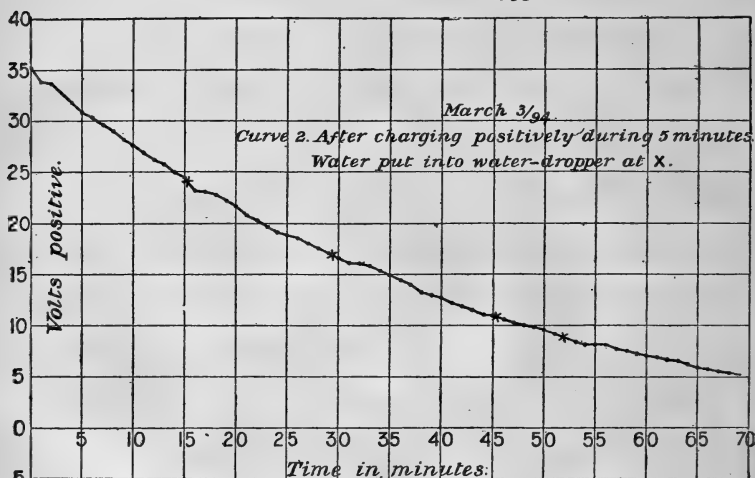
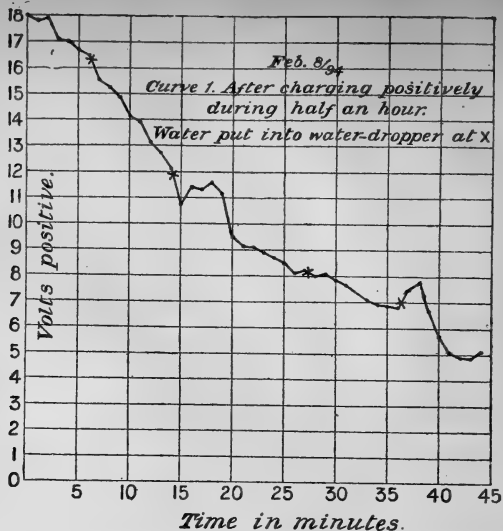
difference of potential between the water-dropper and the vat. The sensibility of the electrometer was 21 scale-divisions (half-millimetres) per volt; and as the scale was 90 centim. long, difference of potentials up to 43 volts, positive or negative, could be read by adjusting the metallic zero to the middle of the scale. A frictional plate-electric machine was used, and by means of it, in connexion with the pin-point, the air inside the vat could be electrified either positively or negatively.

§ 7. The vat was fixed in position in the Apparatus Room of the Natural Philosophy Department of the University of Glasgow on the 13th of December, 1893, and for more than three months the air inside was left undisturbed except by discharges from the pin-point through the electrifying wire, and by the spray from the water-dropper. Thus the air was becoming more and more freed of dust day by day. Yet at the end of the four months we found that the air was as easily electrified, either positively or negatively, as it was at the beginning; and that if we electrify it strongly by turning the machine for half-an-hour, it retains a considerable portion of this electrification for several hours.

§ 8. Observations were taken almost daily since the 13th December; but the following, taken on the 8th of February, the 12th of March, and the 23rd of April, will serve as specimens, the results being shown in each case by a curve. At all these dates the air must have been very free from dust. Both during the charging and during the observations the case of the electrometer and one pair of quadrants are kept metallically connected to the vat. During the charging the water-dropper and the other pair of quadrants were also kept in connexion with the vat. Immediately after the charging was stopped the charging wire was connected metallically to the outside of the vat, and left so with its sharp point unchanged in its position inside the vat during all the observations.

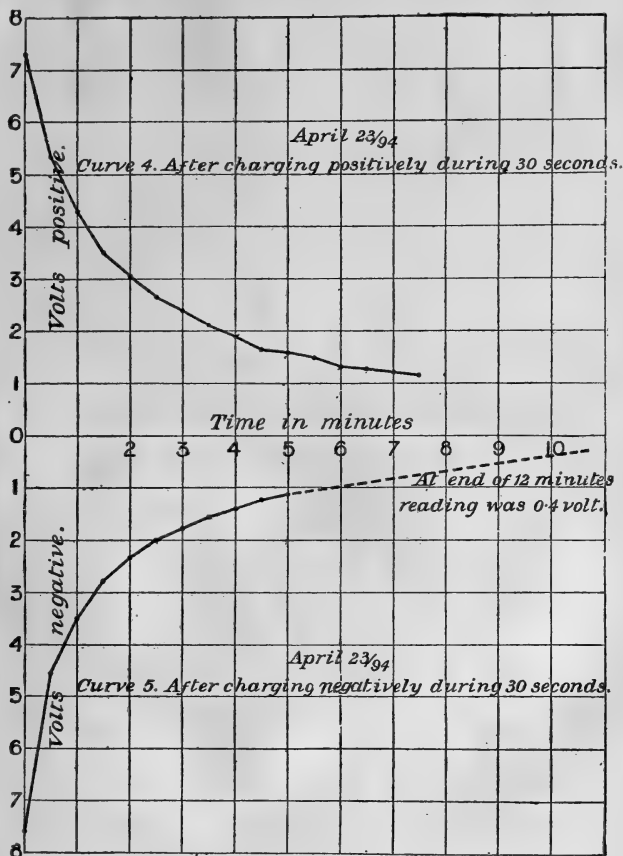
§ 9. *Curve 1. February 8, 1894.*—The friction-plate machine was turned positive for half-an-hour. Ten minutes after the machine stopped the water-dropper was filled and joined to one pair of quadrants of the electrometer, while the other pair was joined to the case of the instrument. The first reading on the curve was taken four minutes afterwards, that is fourteen minutes after the machine stopped running (18 volts).

*Curve 2. March 3, 1894.*—The friction-plate machine was turned positive for five minutes. The water-dropper was filled and joined to the electrometer immediately after the



machine stopped turning. The spot was off the scale, and nine minutes elapsed before it appeared on the scale. The first reading on the curve was taken one minute afterwards, or ten minutes after the machine stopped turning (35.25 volts).

Curve 3. March 12, 1894.—A Voss induction-machine was joined to the charging wire, and run by an electric motor



for 4 hours 19 minutes. A test was applied at the beginning of the run to make sure that it was charging negatively; and a similar test when it was disconnected from the charging wire in the vat showed it to be still charging negatively. The water-dropper was joined to the electrometer, and the spot appeared on the scale immediately. The first reading on the curve was taken half a minute after the machine was disconnected (30.65 volts)

*Curve 4. April 23, 1894.*—The friction-plate machine was turned positive for 30 seconds, with water-dropper running and joined to the electrometer. 20 seconds after the machine stopped the spot appeared on the scale, and the reading  $1\frac{1}{2}$  minutes after the machine stopped turning is the first point on the curve (7·3 volts).

*Curve 5. April 23, 1894.*—The friction-plate machine was turned negative for 30 seconds, with the water-dropper running and joined to the electrometer. 10 seconds afterwards the spot appeared on the scale, and the reading 70 seconds after the machine stopped turning is the first point on the curve (7·6 volts).

The curves show, what we always found, that the air does not retain a negative electrification so long as it retains a positive. We also found, by giving equal numbers of turns to the machine that the immediately resulting difference of potential between the water-dropper and the vat was greater for the negative than for the positive electrification; though the quantity received from the machine was probably less in the case of the negative electrification, because the negative conductor was less well insulated than the positive.

§ 10. On the 21st of March, two U-tubes were put in below the edge of the vat, one on either side, so that it might be possible to blow dusty, or smoky, or dustless air into the vat. To one tube was fitted a blowpipe-bellows, and by placing it on the top of a box in which brown paper and rosin were burning, the vat was filled with smoky air. Again, several layers of cotton-wool were placed on the mouth of the bellows, so as to get dustless air into the vat. The bellows were worked for several hours on four successive days, and we found no appreciable difference (1) in the ease with which the air could be electrified by discharges from the wire connected to the electric machine, and (2) in the length of time the air retains its electrification.

But it was found that, as had been observed four years ago with the same apparatus\*, with the water-dropper insulated and connected to the electrometer, and no electrification of any kind to begin with, a negative electrification amounting to four, five, or six volts gradually supervened if the water-dropper was kept running for 60 or 70 minutes, through air which was dusty, or natural, to begin with. It was also found, as in the observations of four years ago, that no electrification of this kind was produced by the dropping of the water through air purified of dust.

The circular bend of the tube of the water-dropper shown

\* Maclean and Goto, 'Philosophical Magazine,' August 1890.

in the drawing was made for the purpose of acting as a trap to prevent the natural dusty air of the locality from entering the vat when the water-dropper ran empty.

§ 11. The equilibrium of electrified air within a space enclosed by a fixed bounding surface of conducting material presents an interesting illustration of elementary hydrostatic principles. The condition to be fulfilled is simply that the surfaces of equal electric "volume-density" are surfaces of equal potential, if we assume that the material density of the air at given temperature and pressure is not altered by electrification. This assumption we temporarily make from want of knowledge; but it is quite possible that experiment may prove that it is not accurately true; and it is to be hoped that experimental investigation will be made for answering this very interesting question.

§ 12. For stable equilibrium it is further necessary that the electric density, if not uniform throughout, diminishes from the bounding surface inwards. Hence if there is a portion of non-electrified air in the enclosure, it must be wholly surrounded by electrified air.

§ 13. We may form some idea of the absolute value of the electric density, and of the electrostatic force in different parts of the enclosure, in the electrifications found in our experiments, by considering instead of our vat a spherical enclosure of diameter intermediate between the diameter and depth of the vat which we used. Consider, for example, a spherical space enclosed in metal of 100 centim. diameter, and let the nozzle of the water-dropper be so placed that the stream breaks into drops at the centre of the space. The potential shown by the electrometer connected with it, being the difference between the potentials of the air at the boundary and at the centre, will be the difference of the potentials at the centre due respectively to the total quantity of electricity distributed through the air and the equal and opposite quantity on the inner boundary of the enclosing metal; and we therefore have the formula:—

$$V = 4\pi \int_0^a \rho \left( \frac{r^2}{r} - \frac{r^2}{a} \right) dr,$$

where  $V$  denotes the potential indicated by the water-dropper,  $a$  the radius of the spherical hollow, and  $\rho$  the electric density of the air at distance  $r$  from the centre. Supposing now, for example,  $\rho$  to be constant from the surface to the centre (which may be nearly the case after long electrification as performed in our experiments), we find  $V = \frac{2}{3}\pi\rho a^2$ ; whence  $\rho = 3V/2\pi a^2$ .

To particularize further, suppose the potential to have been 38 volts or 0.127 electrostatic C.G.S. (which is less than the greatest found in our experiments) and take  $a=50$  centim.: we find  $\rho=2.4 \times 10^{-5}$ . The electrostatic force at distance  $r$  from the centre, being  $\frac{4}{3} \pi \rho r$ , is therefore equal to  $10^{-4} r$ . Hence a small body electrified with a quantity of electricity equal to that possessed by a cubic centimetre of the air, and placed midway ( $r=25$ ) between the surface and centre of the enclosure, experiences a force equal to  $2.4 \times 10^{-9} 25$ , or  $6 \times 10^{-8}$ , or approximately  $6 \times 10^{-5}$  grammes weight. This is 4.8 per cent. of the force of gravity on a cubic centimetre of air of density  $1/800$ .

§ 14. Hence we see that, on the supposition of electric density uniform throughout the spherical enclosure, each cubic centimetre of air experiences an electrostatic force towards the boundary in simple proportion to distance from the centre, and amounting at the boundary to nearly 10 per cent. of the force of gravity upon it; and electric forces of not very dissimilar magnitudes must have acted on the air electrified as it actually was in the non-spherical enclosure used in our experiments. If natural air or cloud, close to the ground or in the lower regions of the earth's atmosphere, is ever, as in all probability it often is, electrified to as great a degree of electric density as we have found it within our experimental vat, the natural electrostatic force in the atmosphere, due as it is, no doubt, to positive electricity in very high regions, must exercise an important ponderomotive force quite comparable in magnitude with that due to difference of temperatures in different positions.

It is interesting to remark that negatively electrified air over negatively electrified ground, and with non-electrified air above it, in an absolute calm, would be in unstable equilibrium; and the negatively electrified air would therefore rise, probably in large masses, through the non-electrified air up to the higher regions, where the positive electrification is supposed to reside. Even with no stronger electrification than that which we have had within our experimental vat, the moving forces would be sufficient to produce instability comparable with that of air warmed by the ground and rising through colder air above.

§ 15. During a thunderstorm the electrification of air, or of air and the watery spherules constituting cloud, need not be enormously stronger than that found in our experiments. This we see by considering that if a uniformly electrified globe of a metre diameter produces a difference of potential of 38 volts between its surface and centre, a globe of a kilometre

diameter, electrified to the same electric density, reckoned according to the total electricity in any small volume (electricity of air and of spherules of water, if there are any in it), would produce a difference of potential of 38 million volts between its surface and centre. In a thunderstorm, flashes of lightning show us differences of potential of millions of volts, but not perhaps of many times 38 million volts, between places of the atmosphere distant from one another by half a kilometre.

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XXV. *Preliminary Note on the Spectrum of the Electric Discharge in Liquid Oxygen, Air, and Nitrogen.* By Professors LIVEING and DEWAR\*.

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IN making the experiments here described we desired, if possible, to observe the emission-spectra of the several substances, stimulated by the electric discharge, while at temperatures of  $180^{\circ}$  to  $200^{\circ}$  below zero. It seemed probable that the characters of these spectra would give some indications of the physical state of the substances operated on.

In order to prevent the rapid heating of the electrodes by the discharge, they were made of considerable size. One was a disk of platinum about one centimetre in diameter, convex on one side, and having its convexity turned towards the other electrode, which was made of a piece of platinum wire about two millimetres thick. Even these electrodes were much heated, became red-hot when they were not in the liquid, but the spark passed through the gas immediately above the liquid. When actually immersed in the liquid they could hardly have been, except locally at the point of discharge, at any temperature sensibly different from that of the liquid. Experiments were made also with electrodes of aluminium, but with no different results as regards the spectrum except the introduction of the shaded bands due to alumina instead of the lines of platinum.

The liquids experimented on were contained in double test-tubes of large dimensions, having the space between the two tubes highly exhausted. The electrodes, insulated, except at the extremities, by glass tubing and wax or gutta-percha, were passed through a rubber-stopper which closed the tube. Through this stopper was also passed a glass tube, which was left open while experiments were made at the atmospheric pressure, but was connected with a powerful rotary air-pump when it was desired to exhaust the gas in the tube.

\* Communicated by the Authors.

Liquid oxygen, air, and nitrogen, like non-electrolysable compound liquids, offer very great resistance to the passage of an electric discharge, so that with a powerful induction-coil we could hardly make the spark pass through a thickness of one millimetre of liquid. When the thickness of liquid traversed was less than this, a succession of sparks could be maintained; but the resistance appeared to be very great, and the disruptive effect on the electrodes sufficient to discolour the liquid by the particles thrown off their surfaces.

The discharge through the liquid in all cases gave a continuous spectrum and some bright lines traceable to the electrodes, while the rays which we suppose to have been emitted by the molecules of the liquid were less conspicuous. It seems not unlikely, therefore, that the continuous spectrum was due to the particles thrown off the electrodes.

### *Liquid Oxygen.*

When both electrodes were immersed in liquid oxygen boiling at atmospheric pressure, and therefore at about  $-180^{\circ}$  C., and the distance between the electrodes about one millimetre or less, the spectrum of the spark, without jar, was chiefly a continuous one, brightest in the yellowish-green but extending for some distance both on the red and on the blue side. The absorption-bands of oxygen were conspicuous on this bright background. A few bright lines were also seen, of which the most prominent were three in the green and yellowish-green, with the approximate wave-lengths 505, 533, and 547. These lines were not much brighter than the continuous spectrum. Glimpses of other lines were seen, but too faint and intermittent to be measured. Of these lines that with wave-length about 533 is no doubt due to oxygen, for it is described as a triple line of the discharge in vacuum oxygen tubes by Piazzzi Smyth, and as a double line by Schuster. The other two lines appear to be lines of platinum, 5059 and two lines 5475, 5478, according to Thalén.

The introduction of a Leyden jar into the circuit increased the brilliance both of the continuous spectrum and of the lines, or of some of them, and brought out some additional lines; but the intermittent character of the sparks made it almost impossible to measure the places of any of the lines.

When the discharge from a Wimshurst machine was used instead of that from the coil, only a continuous spectrum, with the usual oxygen absorptions, was seen. No bright lines could be detected on the continuous spectrum.

By keeping only the lower electrode (the convex disk) immersed in the liquid, so that the spark passed partly



through the liquid and partly through the gas immediately above it, the discharge took place more easily, and the continuous spectrum became, relatively to the lines, less bright. Without the jar, however, the spectrum had generally the same character as before. The three lines above mentioned were still the most conspicuous bright lines. On putting the jar into the circuit, however, many more bright lines came out. The well-known orange line of oxygen,  $\lambda 6171$ , appeared expanded into a band with its sharper edge on the more refrangible side at a wave-length of about 615, and fading towards the red but traceable as far as  $\lambda 618$ . Schuster and Piazzzi Smyth give a compound line at about wave-length  $\lambda 6156$ ; and it is possible that this band may represent this compound line. It will be noticed that, as to the shading, it follows the character of A and B, but with the dispersion we used it was not possible to resolve it into lines. Probably, under the circumstances, the lines of which we may suppose the band composed would be so much expanded as to overlap one another. Besides this band, blue lines were conspicuous at wave-lengths about 435, 441, 459, 465, 470, all corresponding to known lines of oxygen. The green line of platinum at wave-length about 530 came out brightly, as well as platinum lines at about  $\lambda 583$  and  $\lambda 580$ . Another line, less bright, appeared at wave-length about 557, and at times a second line near it at about 555. These have not been described as oxygen lines by other observers, but they fall within one of the green bands described by Schuster as seen in the negative glow in a vacuous oxygen tube.

We next proceeded to exhaust the gas above the liquid in the vessel, until the pressure was reduced to about 1 centim. of mercury. The liquid, of course, boiled away fast until the temperature had fallen to something like  $-200^{\circ}$ ; and the gas at the reduced pressure offered comparatively little resistance to the passage of the discharge.

So long as both electrodes were immersed in the liquid, the reduction of pressure and of temperature did not make any marked difference in the appearance of the spectrum. But as the liquid evaporated and only the lower electrode was immersed, so that the discharge was partly through the gas, the continuous spectrum was much weakened, and two bright green bands came out extending from about  $\lambda 521$  to  $\lambda 531$ , and from about  $\lambda 553$  to  $\lambda 561$ . This was without a jar in the circuit. The bands were nearly uniformly bright with both edges diffuse. They were much better seen when both electrodes were out of the liquid, and were brightest in the glow which surrounded the poles. They were equally well

seen in the glow about both poles, and equally well when the electrodes were cold, and when they were hot, even red-hot. There was a third much fainter band in the orange a little less refrangible than the D lines of sodium. There is no doubt that these bands are the same as have been described by Schuster in the negative glow in a vacuous oxygen-tube.

When a jar was put in the circuit, these bands disappeared or nearly so. While one electrode remained in the liquid, a good many bright lines came out on putting the jar into the circuit. One of these was a line at wave-length about 557, the same as previously seen, nearly in the middle of one of the green bands. In fact, it seemed to replace the band when the jar was put into the circuit. It was not, however, so permanently seen as some of the other lines. Only a few of these other lines were measured. One appeared to be an oxygen line at about  $\lambda$  544; a pair at about  $\lambda$  566 may have been air-lines as the oxygen usually contains a little air. Another was a platinum line about  $\lambda$  455.

The line above mentioned,  $\lambda$  557, appears to be of some interest because it falls very near the place of the auroral line, and the conditions under which it is produced resemble, in regard to the low temperature, and to some extent in regard to the pressure, those in which Auroras are produced. The place of this line was measured several times, but the circumstances of these experiments were not very favourable for exact measurements. The measure which we marked as the best gave a wave-length for the line 5572, but other measures gave figures between that and 5578. It seems, therefore, not improbable that this line may be identical with the auroral line, of which the exact wave-length cannot even now be said to be quite certainly determined, but which has probably the value 5571.

The identity of the line we have observed with the auroral line cannot be said to be proved as yet. Further observation is needed, and we hope to carry our experiments further. The broad green bands do not seem to be connected with a low temperature, but were produced by the discharge without a jar; this line was, so far as we observed, only produced when one electrode was immersed in the liquid, and therefore cold, and when a jar was in circuit.

The passage of the discharge through the liquid produced much ozone. Not only was the smell of ozone very strong, but the liquid took the indigo tint, deeper than the blue of ordinary oxygen, which is characteristic of ozone. On one occasion, after the sparks had been passed through the liquid for a short time, an explosion ensued which shattered the

vessel. We can assign no cause for this, unless it were an explosion of ozone.

### *Liquid Air.*

The effects of a discharge through liquid air were very similar to those produced with liquid oxygen, so long as the pressure was that of the atmosphere, and no jar was in circuit. There was the same continuous spectrum. When a jar was used a much larger number of lines, generally resembling the ordinary air-lines, were seen but not measured. When the pressure was reduced, the usual banded spectrum of nitrogen was seen, and was strong relatively to the spectrum of oxygen. As the liquid evaporated, and thereby lost more nitrogen than oxygen, the two green bands due to oxygen appeared to become stronger actually as well as relatively to the nitrogen bands.

In this case the discharge produced oxides of nitrogen, which were detected in the residual gas when the air had all evaporated.

### *Liquid Nitrogen.*

We next tried liquid nitrogen. At the pressure of the atmosphere, both electrodes in the liquid, and no jar, the spectrum was continuous with three bright lines in the green and yellowish-green, generally resembling the three lines seen in liquid oxygen. On taking measures of their wave-lengths it was found that they were platinum lines, the same as had been seen in oxygen at wave-lengths about 505, 530, and 547. The oxygen line at 533 was not seen. Besides these three lines, a faint very diffuse line was observed at about  $\lambda$  501, and glimpses of blue bands of the usual banded spectrum of nitrogen. When only one electrode was immersed in the liquid, the line at about  $\lambda$  501 was more distinct. We have no doubt that this represents the strong double line of nitrogen in that position. When the jar was in the circuit, the spectrum was a series of bright lines similar to those given by gaseous nitrogen at atmospheric pressure.

When the gas above the liquid was pumped out until the pressure fell to about 1 centim. of mercury, one or both electrodes being immersed, and no jar used, the band-spectrum of nitrogen appeared. On putting on the jar this was replaced mainly by the line-spectrum.

### *Spectrum of the Spark in Water.*

For the sake of comparison we next observed the spectrum of the spark between platinum electrodes in distilled water at the ordinary temperature and pressure. When no jar was

used the spectrum was continuous, with the red line (C) of hydrogen conspicuous, and the F line just visible, and glimpses of the three platinum lines in the green and yellowish-green. When the jar was put into the circuit the hydrogen lines became very diffuse, but the platinum lines came out much more distinctly, and the readings proved their identity. There were no lines which we could identify with oxygen lines.

The water became quite brown with the particles thrown off the platinum wires used as electrodes.

## XXVI. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 157.]

February 7th, 1894.—W. H. Hudleston, Esq., M.A., F.R.S.,  
President, in the Chair.

MR. C. J. ALFORD, F.G.S., in explanation of specimens of auriferous rocks from Mashonaland exhibited by him, stated that several of them were vein-quartz occurring as segregations in the slates, generally forming veins between the cleavage-planes. Another specimen was a mass of chromate of lead, with pyromorphite and other lead minerals, occurring in masses in decomposed and dislocated talcose slate in the Penhalonga Mine near Umtali, and probably resulting from the alteration of masses of galena by weathering, as a broken vein of galena was found in close proximity. This Crocoisite was supposed to be a somewhat rare mineral, but he had found it and also the native red oxide, Minium, in several places in South Africa. The most interesting specimen was, however, a mass of Diorite showing visible gold throughout the rock, an assay of which gave upwards of 130 ounces of gold per ton. From information obtained from the prospector who made the discovery, he gathered that the deposit was a dyke of Diorite running for a considerable distance, about 8 feet in width, flanked on one side by granite and on the other by slates. There were extensive ancient workings extending to a depth of about 60 feet, and the prospecting shafts had not gone much below that depth, so not much information was obtainable at present. The Diorite showed a development of Epidote, but little or no quartz; and the gold appeared to enter in an extraordinary manner into all of the composing minerals. Mr. Alford hoped, after his next visit to Mashonaland, to be in a position to lay before the Society more definite information regarding these interesting rocks.

The following communications were read:—

1. 'On some cases of the Conversion of Compact Greenstones into Schists.' By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S.

By the path leading from the Bernina Hospice to the Grüm Alp

(Engadine) some masses of compact green schist are seen, intercalated in a rather crushed gneiss. They prove to be intrusive dykes modified by pressure. Microscopic examination of specimens from these reveals no trace of any definite structure indicating an igneous rock; a slice, cut from one of the masses within an inch or so of a junction, shows it to be a foliated mass of minute chlorite or hydrous biotite, with granules of epidote (or possibly some sphene) and of a water-clear mineral, perhaps a secondary feldspar. An actual junction shows a less distinct foliation and some approach to a streaky structure. A slide from the middle of another dyke (about 18 inches thick) exhibits a more coarsely foliated structure and minerals generally similar to the last, except that it may contain a little actinolite and granules of hæmatite (?) and the clear mineral, in some cases, seems to be quartz. The structure and most of the minerals appear to be secondary. Chemical analysis shows the rock to have been an andesite. A specimen from a third dyke is generally similar, but is rather less distinctly foliated.

A somewhat similar, but rather larger intrusive mass by the side of the Lago Bianco shows more actinolite and signs of primary feldspar, with other minerals. Here the rock retains some likeness to a diabase. The resemblance of certain of these rocks to somewhat altered sediments is remarkable. The Author considers the bearing of this evidence upon other and larger masses of 'green schist' which occur in the Alps, and expresses the opinion that their present mineral structure may be the result of great pressure acting on more or less basic igneous rocks.

2. 'The Waldensian Gneisses and their Place in the Cottian Sequence.' By J. Walter Gregory, D.Sc., F.G.S.

The lower part of the sequence of the Cottian Alps has been universally divided into three series, of which the lowest has been regarded as a fundamental (basal) Laurentian gneiss. It is the object of the present paper to show that this rock is really intrusive in character and Upper Tertiary in age. The writer endeavours to show this by the following line of argument:—(1) The gneiss consists of only isolated outcrops instead of a continuous band, and these occur at different positions and not always at the base of the schist series; (2) the gneiss is intrusive, because: (a) it includes fragments of the overlying series instead of *vice versa*, (b) it sends off dykes of aplite into the surrounding schists, (c) it metamorphoses the rocks with which it is in contact, and (d) the schists are contorted near the junction; (3) the gneisses are further shown to be later than the igneous rocks intrusive into the 'pietre verdi' series, as these never traverse the gneiss.

No positive opinion as to the age of the overlying schists is expressed in the paper, though it is pointed out that the recent discovery of radiolarian muds in the series may necessitate their inclusion in the Upper Palæozoic. The freshness of the gneisses, the fact that these have not been affected by the early Tertiary

earth-movements, and the absence of authentic specimens of the gneiss in the Cretaceous, Eocene, and Miocene conglomerates, renders their late Tertiary age highly probable.

The nature of the contact-metamorphism and the origin of the gneissic structure are discussed, and a classification offered of the earth-movements in the Cottian Alps.

February 21st.—Dr. Henry Woodward, F.R.S., President,  
in the Chair.

The following communications were read :—

1. 'On the Relations of the Basic and Acid Rocks of the Tertiary Volcanic Series of the Inner Hebrides.' By Sir Archibald Geikie, D.Sc., LL.D., F.R.S., F.G.S.

After an introductory sketch of his connexion with the investigation of the Tertiary volcanic rocks of Britain, the Author proceeds to describe the structure of the ground at the head of Glen Sligachan, Skye, which has recently been cited by Prof. Judd as affording inclusions of Tertiary granite in the gabbro, and as thus demonstrating that the latter is the younger rock. He first shows that the gabbro, instead of being one eruptive mass, consists of numerous thin beds and sills of different varieties of gabbro, some of which were injected into the others. These various sheets, often admirably banded, can be seen to be truncated by the line of junction with the great granophyre-tract of Glen Sligachan. A large mass of coarse agglomerate is likewise cut off along the same line. These structures are entirely opposed to the idea of the gabbro being an eruptive mass which has broken through the granophyre. They can only be accounted for, either by a fault which has brought the two rocks together, or by the acid rock having disrupted the basic. But there is ample evidence that no fault occurs at the boundary-line.

The granophyre becomes fine-grained, felsitic, and spherulitic along its margin, where it abuts against the complex mass of basic rocks. These structures continue altogether independent of the varying distribution of the gabbros, and are seen even where the granophyre runs along the side of the agglomerate. Similar structures are of common occurrence along the margins of the granophyre-bosses and sills of the Inner Hebrides, being found not only next the gabbro, but next the Jurassic sandstones and shales. They are familiar phenomena of contact in all parts of the world, and are sufficient of themselves to show that the granophyre of Skye must be later than the gabbro.

The Author then describes three conspicuous dykes, from 8 to 10 feet broad, which can be seen proceeding from the main body of granophyre and cutting across the banded gabbros. One of these is traceable for more than 800 feet in a nearly straight line. The material composing these dykes is identical with that constituting the marginal portion of the granophyre-mass. It presents the most exquisite flow-structure, with abundant rows of spherulites. The

Author exhibited a photograph of one of the dykes ascending vertically through the gabbros. Numerous dykes and veins of the same material, not visibly connected with the main granophyremass, traverse the gabbros of the ridge of which Druim an Eidhne forms a part. Some of these are described in the paper, and it is shown that the flow-structure follows the irregularities of the gabbro-walls and sweeps round enclosed blocks of altered gabbro. The 'inclusions' described by Prof. Judd are portions of these dykes and veins. There is not, so far as the Author could discover, a single granite-block enclosed in the gabbro anywhere to be seen at this locality. He therefore claims not only that his original description of the relations of the rocks was perfectly correct, but that the evidence brought forward to contradict it by Prof. Judd furnishes the most crushing testimony in its favour.

2. 'Note on the Genus *Naiadites*, as occurring in the Coal Formation of Nova Scotia.' By Sir J. William Dawson, K.C.M.G., LL.D., F.R.S., F.G.S. With an Appendix by Dr. Wheelton Hind, B.S., F.R.C.S., F.G.S.

March 7th.—Dr. Henry Woodward, F.R.S., President,  
in the Chair.

The following communications were read:—

1. 'The Systematic Position of the Trilobites.' By H. M. Bernard, Esq., M.A., F.L.S., F.Z.S.

2. 'Landscape Marble.' By Beeby Thompson, Esq., F.G.S., F.C.S.

The Cotham Stone is a hard, close-grained, argillaceous limestone with conchoidal fracture. The dark arborescent markings of the stone rise from a more or less stratified dark base, spread out as they rise, and terminate upwards in wavy banded portions of the limestones. In some specimens two 'landscapes' are seen, one above the other, each rising from a distinct dark layer.

The Author describes the microscopical and chemical characters of the rock, and its mode of occurrence, and discusses the explanations which have been put forward to account for its formation, especially that of Edward Owen, who in 1754 gave the first published description of the Cotham Stone, and that advanced by Mr. H. B. Woodward in the 'Geological Magazine' for 1892. He then proposes a new explanation to account for the formation of the rock, and maintains that its peculiar characters are due to interbedded layers of vegetable matter, which decomposed and evolved carbonic-acid gas and marsh-gas. This decomposition continued while several inches of new sediment were laid down, the result being that arborescent markings were produced along the lines taken by the escaping bubbles, and that the upward pressure of these gases, after their escape had been prevented by increasing coherence or greater thickness of the upper layers of sediment, caused the corrugations

in the upper surface of the stone. He further discusses the composition of the stone, and describes experiments which he made to illustrate his views.

3. 'On the Discovery of Molluscs in the Upper Keuper at Shrewley, in Warwickshire.' By the Rev. P. B. Brodie, M.A., F.G.S.

March 21st.—Dr. Henry Woodward, F.R.S., President,  
in the Chair.

The following communications were read:—

1. 'On the Origin of certain Novaculites and Quartzites.' By Frank Rutley, Esq., F.G.S., Lecturer on Mineralogy in the Royal College of Science, London.

The novaculites of Arkansas have already been admirably described by Mr. Griswold in vol. iii. of the Arkansas Survey Report for 1890. One of the characteristic microscopic features in Ouachita stone is there stated to consist in the presence of numerous cavities, often of sharply-defined rhombohedral form, which Mr. Griswold considers to have been originally occupied by crystals of calcite or dolomite.

The Author, while admitting that the cavities were no doubt once filled by the latter mineral, ventures to differ from Mr. Griswold, and some of the authorities he cites, concerning the origin of the rock. Crystalline dolomites, when dissolving, become disintegrated into minute but well-formed rhombohedra. As the process of dissolution proceeds these crystals may become so eroded that the rhombohedral form is no longer to be recognized. The Author points out that no inconsiderable proportion of the cavities in Ouachita stone present irregular boundaries, such as the moulds of partially eroded rhombohedra would show. He then offers a fresh interpretation of these cavities, so far as the origin of the rock is concerned:—

1st. He assumes that beds of crystalline magnesian limestone have been slowly dissolved by ordinary atmospheric agency and the percolation of water charged with carbonic acid or other solvent.

2nd. That, as the limestone was being dissolved, it was at the same time being replaced by silica, which enveloped minute isolated crystals and groups of crystals, some perfect, others in various stages of erosion.

3rd. That the silica assumed the condition of chalcedony, its specific gravity, as stated by Mr. Griswold and as determined by the Author, being low in comparison with that of quartz.

4th. The residuum of the original dolomite or dolomitic limestone was removed, leaving the perfect and imperfect rhombohedral cavities.

A calciferous, gold-bearing quartzite from the Zululand gold-fields is described and a similar origin is ascribed to it, but in this case the original rock appears to have been simply a limestone,



not a dolomite. The gold seems to occur chiefly in the calcareous portions of the rock. The Author has also been tempted to suggest a similar origin for the saddle-reefs of the Bendigo gold-field. In all of these cases the train of reasoning is based upon the conclusions arrived at in his previous paper 'On the Dwindling and Disappearance of Limestones.' He indicates that the stratigraphical relations of the Arkansas novaculites, as described in Mr. Griswold's Report, are such as to warrant the assumption that limestones once occurred in the position now occupied by beds of novaculite. Many collateral matters are dealt with in the paper which cannot be given in abstract: among them is an attempt to classify quartzites.

2. 'Note on the Occurrence of Perlitic Cracks in Quartz.' By W. W. Watts, Esq., M.A., F.G.S.

The Author of this communication described some specimens of the porphyritic pitchstone of Sandy Braes in Antrim, which are deposited in the Museum of Science and Art in Dublin, and in that of Practical Geology in Jermyn Street. They exhibit admirable examples of perlitic structure in the brown glassy matrix and the presence of polygonal, circumferential, and radial cracks is noticed. The porphyritic crystals of quartz are traversed by curved fissures of retreat, not so perfect as those found in the glass, but better than those usually produced by the rapid cooling of Canada balsam. The fissures in the quartz are frequently prolonged into the matrix, undergoing only a very slight and almost imperceptible deviation in direction at the junction. But in addition to this the quartz is often found to act as a centre of strain, the inner cracks of the perlite being wholly in quartz, the next traversing both, and the outer ones in glass only. In other examples the outer cracks of a matrix perlite sometimes enter the quartz, while in others polygonal cracks occur, and join up in, the quartz and give off radial cracks precisely like those of the matrix. These observations lead to the conclusion that the quartz and glass must have contracted at about the same rate, and that the observation of perlitic structure in a rock with trachytic or felsitic matrix by no means proves that the rock is necessarily a devitrified glass. References are given to somewhat similar observations by Fouqué and Michel-Lévy, and by Idings.

## XXVII. *Intelligence and Miscellaneous Articles.*

ON THE THERMAL BEHAVIOUR OF LIQUIDS.

BY PROF. BATTELLI.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

I HAVE been prevented for a considerable time from attending to my usual studies by serious domestic trouble, and thus I was not able at once to read and consider the observations of Professors

Ramsay and Young, in the February number of the *Philosophical Magazine*, on the results obtained by myself and others on the state of matter at the critical point.

In the first place, the authors observe that there are contradictions between the results arrived at by Galitzine, de Heen, and Zambiasi, and those obtained by myself; and these contradictions are reduced in the main to the two following:—

(A) That according to my observations the meniscus disappears during the heating at a temperature higher than the true critical temperature, whilst according to the observations of Galitzine, de Heen, and Zambiasi, the dimness forms during the cooling at a lower temperature than the critical one.

(B) That Zambiasi and I found that the dimness (or cloudiness) during the cooling process is produced at a lower temperature when the substance contained in the experimenting tube is in a larger quantity, whilst de Heen found just the contrary, and Galitzine came to the conclusion that the temperature of the cloudiness is “practically independent of the relative quantity of liquid.”

It will be well to examine more closely what are the foundation and value of these contradictions.

The first does not exist. In fact from the experiments both of Galitzine and myself, in the most favourable conditions the disappearance of the meniscus to the last trace of it occurs at a higher temperature than that which one perceives in the ordinary mode of observation, and the disappearance itself takes place at a higher temperature than that at which the cloudiness afterwards takes place. Whilst also it results from my experiments that the cloudiness takes place at a lower temperature than the true critical temperature, in conformity with the result obtained by the other three observers. That Zambiasi found the temperature of the disappearance of the meniscus coincident with that of the cloudiness, must certainly be attributed to his mode of observing the temperature.

In regard to the second point, on the contrary, the difference exists, and therefore merits fresh experiments in order to arrive at a definitive decision.

I would notice that, in the many observations made by me with several tubes containing various quantities of substance, I had each time a couple of these tubes in identical conditions, and the observation of these tubes was very clear and contemporaneous: therefore it may be that the difference depends on the methods of observation more or less adapted to the end in view, and thus it seems to me that I am right in insisting on my conclusions, which, however, I shall be ready to give up when decisive experiments have settled the question.

The reasons alleged by Professors Ramsay and Young for declaring incorrect the experiments in question, which lead to conclusions differing from their ideas on the point, are the following:—

(1) That in our apparatus we could not have a perfectly uniform temperature;

(2) That we did not make certain of dealing with perfectly pure liquids and entirely deprived of air.

As to the uniformity of the temperature, Signor Galitzine has already replied, in the April number of the Philosophical Magazine, that the criticism regarding him was not well founded.

I can now repeat the same; for I must remind the reader that for heating I used petroleum distilled at determined temperatures, the vapours of which circulated in a stove with double sides, in the interior of which a closed glass globe contained the tubes. The length of these was a little more than the fourth part of the length of the entire globe, and they were placed in the middle of it, in correspondence with the height of the mouth of the tubes which conducted the petroleum-vapour into the stove.

I have already noted that an even temperature was preserved in the stove up to exactly  $\frac{1}{10}$  degree for ten or fifteen minutes beforehand, and sometimes even for a longer period; thus it is absolutely impossible to suppose that there was not a uniform temperature in the globe, and especially in the small space occupied by the little tubes.

As regards the absolute purity of the liquids and the entire absence of air, one cannot perhaps give a categorical reply; from all the memoirs on the subject, however, it would appear the greatest care was taken to that end by every experimentalist.

But admitting that the apparent difference depends on the impurity of the substance or on the presence of air, still one could not altogether impugn the conclusion at which we have arrived.

In fact one could not explain merely by the hypothesis of Andrews the fact described in § 7 of my first memoir (*Nuovo Cimento Genov.* for Feb. 1893), namely, that in two bulbs placed in a stove at the same height, and connected by a small capillary tube in the form of a  $\cap$ , one of which contains liquid ether and not the other, when they become heated above the critical temperature, and then slowly cool, the characteristic cloudiness appears only in the bulb which originally contained the liquid. Nor, according to the same hypothesis, would the conduct of the isocores in regard to the critical temperature be as it is in reality, as I demonstrated in § 10 of the same memoir.

Finally, the fact observed by Galitzine (*Wied. Ann.* vol. 50. p. 541) is in contradiction to the ideas of Messrs. Ramsay and Young, namely, that if the two branches of a tube are separated at the U by a little column of mercury, and the one branch is filled entirely with ether and the other partially, when the tube becomes heated above the critical temperature the movement of the column of mercury from the first branch towards the second does not cease, even if the temperature is increased to  $209^{\circ}5$  C.

I was proving the same thing when Galitzine's paper appeared, using for this purpose a straight tube instead of a curved one, and

the observations were most carefully made, and some of them were repeated by Messrs. Cagnato and Strapazzon.

The result arrived at by me is considered incorrect by Messrs. Ramsay and Young—that “the vapour-pressure at a given temperature depends on the relative volumes of liquid and gas,” because it is “absolutely opposed” to their experiments, and they thus maintain that my liquids must have contained some other liquid, or that they contained a permanent gas.

But I reply that the memoirs which describe my experiments detail all the minute care taken by me in order to obtain pure liquids; and they also give the calculation (in the case of ether and of carbonic sulphide) which shows that the increase of pressure could not be attributed to gas which might casually have remained in the experimental globe.

I would rather observe that, in order to observe such a phenomenon, an apparatus is necessary which enables us—as in my case—slowly to compress the vapour, and to maintain it for a time under constant pressure.

#### ON THE FORMATION OF FLOATING METAL LAMINÆ.

BY F. MYLIUS AND O. FROMM.

The following are the results of this investigation :—

1. Oxidizable metals such as zinc, iron, cobalt, cadmium, copper, silver, and antimony, have the property that when separated by electrolysis they float on the surface of solutions of their salts in coherent laminæ.

2. This diffusion depends on two circumstances—firstly, the presence of an impurity which does not mix with water; and, secondly, the chemical action of the oxygen present. The same effect is produced by sulphur on the halogens.

3. For the spreading of the metals on the boundary of two media, the thickness of the oily layer is not of essential importance.

4. The form of the bounding surface has no appreciable influence on the phenomenon: hence the spreading occurs even when one medium is in the form of drops.

5. Oxides and sulphides which conduct the current have the property of spreading out on the bounding surface; thus, for instance, the lower degrees of oxidation of silver and of cadmium, peroxide of lead, subsulphide of copper.

6. The growth of the floating laminæ is influenced by the capillary attractions which those parts of the liquid experience from which the precipitate is deposited.

7. During the passage of the current a tension is often observed which disappears when the current is broken, and apparently depends on the difference of potential, like the surface-tension of mercury when it is polarized.—Wiedemann's *Annalen*, No. 4, 1894.

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AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

SEPTEMBER 1894.

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XXVIII. *On the Velocity of Sound in Air, Gases, and Vapours for Pure Notes of different Pitch.* By J. WEBSTER LOW, *Ph.D., B.A.\**

§ 1. *Introduction.*

BY the publication of Regnault's† great work and the immediate corroboration of his results by Le Roux‡, the general confidence in the previously accepted value of the velocity of sound was severely shaken. Since then several experimenters have sought, by measuring the wave-lengths of notes of different pitch, to arrive indirectly at the velocity of sound. With this object Kundt§ and Kayser|| have utilized the former's dust-figures, Schneebeli¶ and Seebeck\*\* Quincke's interference-tubes††; and all have agreed in finding a greater velocity for the higher notes than for the lower ones, a result the reverse of that found by Regnault and König‡‡.

From theoretical considerations, Helmholtz§§ and Kirchhoff||| have shown that friction and the conduction of heat

\* Communicated by the Author.

† *Compt. Rend.* lxi. pp. 209-220; *Mém. de l'Inst.* xxv. (1867).

‡ *Ann. de Chem.* 4 série, xii. pp. 345-418.

§ *Pogg. Ann.* cxxvii. p. 497 (1866); and cxxxv. pp. 337-372 and 527-561 (1868).

|| *Wied. Ann.* ii. pp. 218-241 (1877); and vi. p. 465 (1879).

¶ *Pogg. Ann.* cxxxvi. p. 296 (1869).

\*\* *Pogg. Ann.* cxxxix. p. 104 (1870).

†† Quincke, *Pogg. Ann.* cxxviii. p. 177 (1866).

‡‡ König, *Mém. de l'Inst.* xxxvii. p. 435.

§§ *Verhandlungen des natur.-histor. medicin. Vereins zu Heidelberg vom Jahre* 1863, iii. p. 16.

||| *Pogg. Ann.* cxxxiv. p. 177 (1868).

*Phil. Mag.* S. 5. Vol. 38. No. 232. Sept. 1894.

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must greatly affect the wave-length and the velocity of sound in narrow tubes. Their theory agrees only imperfectly with the results of Kundt, who employed mixed notes; with those of Schneebeli, Seebeck, and Kayser, however, all of whom used pure musical tones, the accord is somewhat better. The methods of the last named inquirers, though correct in principle, are, however, in detail liable to various objections; I have therefore subjected the whole question of the indirect determination of the velocity of sound to a fresh investigation.

The questions I set myself for answer were:—

1. How does the velocity of sound vary in air and gases for pure notes of different pitch in tubes of different diameter?
2. How can the true velocity of sound in unlimited space be determined from that found in tubes?

### § 2. *Method of the Inquiry.*

At the suggestion of Prof. Quinke I measured the wave-lengths for tuning-forks of known vibration-frequency by means of his interference-tubes. I observed, not one minimum of vibration-intensity, as Seebeck had done, but successive maxima, by shortening the tubes by one, two, or more half wave-lengths. My apparatus (fig. 1) consisted of a wide glass tube O U, closed at the bottom with a cork and a stop-cock H. From H a long piece of guttapercha tubing led to a water-bottle F; a second piece of narrower tubing connected the side-tube A, distant about 5 centimetres from the upper end of the main tube, with the ear of the observer at C, ending in a glass pipe coated with sealing-wax, so as to fit exactly into the outer passage of the ear. By raising and lowering the bottle F a swimmer B could be brought to any desired point of the interference-tube, and the exact position of its upper smooth surface could be read off on a millimetre-scale fixed behind the tube. The swimmer consisted of a cork 4 centim. long, loaded at the lower end with lead and coated with stiff paper and paraffin. The cork had almost the same diameter as the tube.

The theory of vibrating air-columns, as developed by Kirchhoff, postulates a regular motion of the air-particles parallel to the axis of the tube. In the course of my experiments, however, whether the bare prong or the resonance-box of the tuning-fork was held over the opening of the tube, or the fork-handle pressed firmly against any point of its sides, or the fork, with box attached, removed to any part of the room, I failed to observe any change in the positions of the maxima. These positions could, however, be most easily

and distinctly found by using the flat side of the bare prong. Some of the earliest readings were taken with the resonance-box; but I soon laid it aside, as the strong resonance of the box obscured too much the maximum of resonance of the tube.

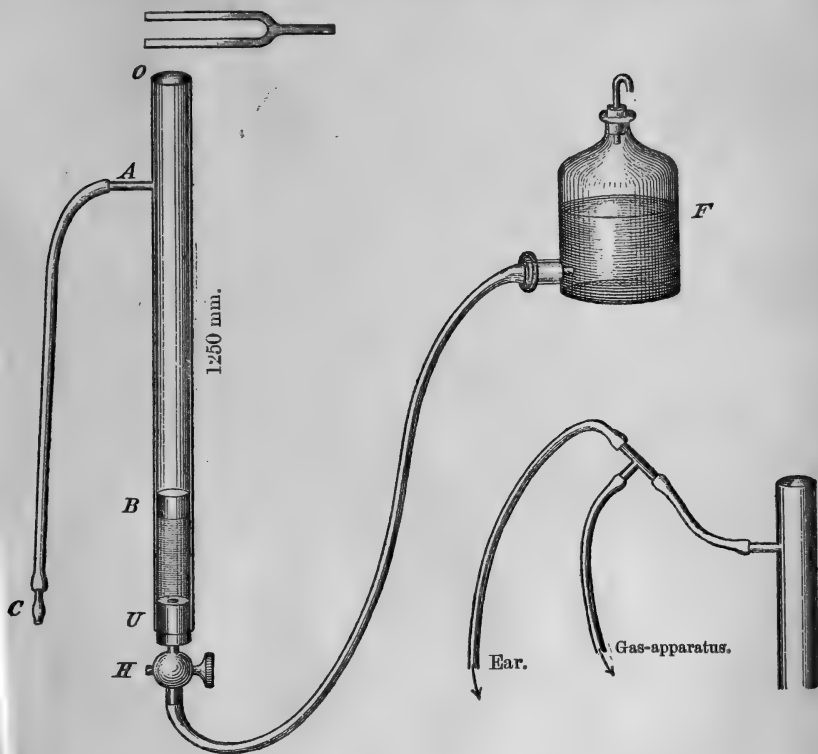


Fig. 1.

Fig. 2.

In a tube like that represented in fig. 1 the air-column can resonate in two different ways. In the one case a loop forms at the side-piece A, and a minimum of intensity is heard through the tubing A C. The distance of the loop from the reflecting surface of the swimmer is then an odd multiple of a quarter wave-length. Raise the swimmer through a distance equal to the length A O, increased by the amount of Rayleigh's correction\* for open pipes, then a loop forms at O, a greater change of density takes place at A, and a maximum of intensity is heard through A C. The distance of the

\*  $+0.82 \times \text{radius of the pipe.}$  Vide Lord Rayleigh's 'Sound,' vol. ii. § 307, and Appendix A.

swimmer now from the end O, increased by Rayleigh's correction, is an odd multiple of a quarter wave-length. The difference between two successive maxima or minima is thus half a wave-length. After careful trial I found that the maxima, at all events for my ear, could be fixed with much greater precision than the minima.

From the observed half wave-length,  $v_0$ , the velocity of sound in dry air at  $0^\circ$  temperature and 760 millim. pressure was calculated by means of the formula

$$v_0 = 2n \frac{\lambda}{2} \left( 1 - \frac{\alpha t}{2} - \frac{3}{16} \frac{S}{B} \right);$$

where

$n$  = the vibration-frequency of the fork,

$\lambda$  = the observed wave-length,

$\alpha$  = the coefficient of expansion of air,

$t$  = the temperature of the air in degrees Cent.,

$S$  = the vapour-tension of water,

and  $B$  = the barometric height.

Any influence of the intensity or *vis viva* of vibration upon the velocity of sound, which Regnault\* thought he had discovered, but which Rink† has with justice disputed, I could not observe. Kundt\* also and Kayser\* have found the velocity of sound invariable for different degrees of vibration-energy of the sounding body.

In making my observations I proceeded in the following manner:—With the water-bottle in the hand I raised and lowered the swimmer a few times until I had with tolerable certainty ascertained the positions of the maxima. More than one reading of the same maximum at the same time I never took; I rather returned to it four or five times in order to get my observations as independent of one another as possible.

The temperature was observed above and below at the beginning and the end of each experiment.

The tuning-forks  $c_p$ ,  $e_p$ ,  $g_p$ ,  $c_{II}$ ,  $c_{III}$  were all made by König, of Paris. The vibration-frequencies of the first four were found to be in the ratio of 4 : 5 : 6 : 8, but  $c_{III}$  made 1023·25 vibrations when  $c_{II}$  made 512.

I used three different tubes, which were of the same length, 1250 millim., and of which the diameters were 28 millim., 17·1 millim., and 9·35 millim.

In order to convey a clear idea of the degree of precision of which the method is capable, I shall quote the details of a

\* Regnault, Kundt, Kayser (see footnotes, *ante*, p. 249).

† Pogg. *Ann.* cxlix, p. 546 (1873).



single experiment taken at random from my journal. This was one of a series made at the beginning of the inquiry, when I had joined two tubes together in order to follow the maxima as far down into the tube as possible. As was to be expected on account of the decreasing intensity, the readings became more difficult the farther they were removed from the source of sound. After convincing myself in this way that the wave-length remained constant, I determined only the uppermost maximum and the lowermost that could be distinctly observed, divided their difference by the number of half wave-lengths contained in the interval passed through, and arrived in this way at the mean half wave-length.

Fork $c_{\text{m}}$ $n$ . . . .	= 512.
Tube II., diameter . .	= 17.1 millim.
Mean temperature . .	= 12°·3 C.
Vapour-tension . . .	= 10.5 millim.
Barometric height . .	= 754 millim.

## Readings for the Maxima.

Temp. C.	1.	2.	3.	4.	5.	6.	7.
	millim.	millim.	millim.	millim.	millim.	millim.	millim.
12	157	483	811	1136	1464	1792	2122
12.3	157	484	812	1138	1466	1793	2119
12.3	156.5	484	811	1139	1466	1792	2121
12.7	157.5	485	812	1140	1467	1794	2121
Mean 12.3	157*	484	811.5	1137.7	1466.3	1792.7	2120.7

## Half Wave-lengths.

## Velocity.

327 millim.	326.3 metre.
327.5 „	326.9 „
326.2 „	325.6 „
328.6 „	327.8 „
326.4 „	325.8 „
328 „	327.4 „

Mean ..... 326.6 „

\* The first quarter wave-length in the above experiment, increased by Rayleigh's correction (157+0.82 radius), gives a velocity of 327.4 metre. I very often calculated the velocity in this way, and always found nearly the same value as from the other readings. Such values were, however, never included in the mean.

From the above figures it is plain that the method, even for a tyro, makes considerable pretensions to exactness ; after many months of practice, however, the limits of error became still closer.

Table showing the observed Mean Velocities in Air.

	Internal diameter of the tube.	$c_1$ $n=256.$	$c_2$ $n=320.$	$c_3$ $n=384.$	$c_{11}$ $n=512.$	$c_{111}$ $n=1023.25.$
I. ....	millim. 28	metre. 327.29	metre. 327.50	metre. 327.69	metre. 328.33	metre. 328.68
II. ....	17.1	325.24	325.54	326.03	326.70	327.80
III. ....	9.35	320.60	321.19	321.88	323.60	325.29

### § 3. Kirchhoff's Formula discussed.

In the light of these results let us test Kirchhoff's\* theoretical formula for the velocity of sound in tubes :—

$$v = a \left( 1 - \frac{\gamma}{2r\sqrt{\pi n}} \right),$$

where

$v$  = the observed velocity in tubes,

$a$  = the velocity in unlimited space,

$r$  = the radius of the tube,

$n$  = the vibration-frequency of the tuning-fork,

and  $\gamma$  = a constant for friction and conduction of heat.

For the same tube the product  $(a-v)\sqrt{n}$  must be constant, as also  $(a-v)2r$  for the same tone.

Then from two results with the same fork and different tubes we get

$$a = \frac{v_1 r_1 - v_2 r_2}{r_1 - r_2},$$

where  $v_1$  and  $r_1$  denote the velocity and the radius of the wider tube,  $v_2$  and  $r_2$  the same quantities for the narrower one. Thus, by combining in pairs the results contained in the vertical columns of the above table, we should always get the true velocity of sound in the open air. My results calculated in this way are as follows :—

\* Pogg. *Ann* cxxxiv. p. 177 (1868); or Kirchhoff's *Ges. Abh.* p. 543.

Tuning-fork.	Tubes I. and II.	Tubes I. and III.	Tubes II. and III.	Mean.
	metre.	metre.	metre.	metre.
$c_i$ .....	330.3	330.6	331.1	330.67
$e_i$ .....	330.3	330.6	330.9	330.60
$g_i$ .....	330.1	330.5	330.9	330.50
$c_{ii}$ .....	330.7	330.7	330.6	330.67
$c_{iii}$ .....	330.3	330.5	330.6	330.47
			Mean .....	330.582

If this be the true velocity of sound in the open, then the values of  $(a-v)2r$  taken vertically in the first of the following tables, and those of  $(a-v)\sqrt{n}$  taken horizontally in the second, should, as required by Kirchhoff's formula, be constant.

TABLE I.  
Values of  $(a-v)2r$ .

Internal diameter of the tube.	$c_i$ $n=256$ .	$e_i$ $n=320$ .	$g_i$ $n=384$ .	$c_{ii}$ $n=512$ .	$c_{iii}$ $n=1023.25$ .
millim. 28	0.09843	0.08626	0.08093	0.06301	0.05321
17.1	9825	8618	7780	6634	4753
9.35	9867	8778	8132	6527	4945

TABLE II.  
Values of  $(a-v)\sqrt{n}$ .

Internal diameter of the tube.	$c_i$ $n=256$ .	$e_i$ $n=320$ .	$g_i$ $n=384$ .	$c_{ii}$ $n=512$ .	$c_{iii}$ $n=1023.25$ .
millim. 28	52.64	55.09	56.62	50.91	60.77
17.1	85.43	90.14	89.15	87.78	88.90
9.35	159.7	168.0	170.4	158.0	169.2

Considering that any error in the observed value of  $v$  becomes greatly magnified in the above numbers, the small deviations from a constant mean are almost negligible. The generally excellent agreement between theory and experiment, when  $a=330\cdot58$  metre, speaks for the correctness of this number as the true value of the velocity of sound.

If with this value we calculate the constant  $\gamma$  for the different tubes, we find the following results :—

Tube.	$e_1$ .	$e_2$ .	$g_1$ .	$e_{11}$ .	$e_{111}$ .
I. ....	0·007902	0·008265	0·008500	0·007642	0·009122
II. ....	7830	8262	8264	8046	8149
III. ....	8002	8418	8543	7916	8480
Mean=0·007989.					

This experimental mean 0·007989 tallies very closely with 0·00742, the theoretical value, calculated by means of Kirchhoff's formula\* from O. E. Meyer's† constant of friction of air and Maxwell's theory of the conduction of heat.

We may also calculate  $k$ , the ratio of the specific heats, by the formula

$$a = \sqrt{\frac{B \cdot Q \cdot g \cdot k}{\Delta_0}},$$

where  $B=0\cdot760$  metre,  $Q=13\cdot596$ ,  $g=9\cdot81$  metre, and  $\Delta_0 = \frac{1}{773}$ .

By substituting these values and putting  $a=330\cdot582$  metre we find

$$k=1\cdot3947,$$

while all previous values lie between 1·419 and 1·3845.

\*

$$\gamma = \sqrt{\mu} + \left( \frac{a}{b} - \frac{b}{a} \right) \sqrt{\nu},$$

where

$a$ =the true value of the velocity of sound in air,  
 $b$ =Newton's " "  
 $\mu$ =a constant for conduction of heat, "  
 $\nu$ =a constant for friction.

Vide Kirchhoff's *Ges. Abh.* p. 543.

† Pogg. *Ann.* xxxii. p. 642.

My results for air may be summed up as follows :—

1. The velocity of sound in narrow glass tubes is smaller than in the open air ; it increases with the diameter of the tube and the pitch of the note.

2. The loss which the velocity of sound suffers in narrow glass tubes is inversely proportional to the diameter and the square root of the vibration-frequency. In other words, the formula

$$a-v = \frac{\gamma}{2r\sqrt{\pi n}}$$

is correct if  $a$ , the true velocity, = 330·582 metre\*, and  $\gamma$ , the constant for friction and conduction of heat, = 0·007989.

3. The ratio of the specific heats for air is 1·3947\*.

#### § 4. Carbonic Acid.

The alteration of the apparatus necessary for the application of this method to gases depends upon the density of the gas.

For carbonic acid everything remained the same as for air, with the exception of a small change at the side-piece A.

As the main tube had to remain open, the chief difficulty lay in keeping the gas pure. The air could either, by diffusion, penetrate into the tube, or, by the lowering of the water-column, be drawn into it. The difficulty was overcome in the following manner.

The three arms of a T (fig. 2) were fitted with pieces of gutta-percha tubing, of which the one led to the side tube A, the other to the gas-apparatus, and the third to the ear of the observer. The T-piece was fixed so high and so inclined to one side, that the heavy gas flowed in a natural manner into the main tube.

The gas was generated in a Kipp's apparatus from oyster-shells and hydrochloric acid, and conducted through a system of wash-bottles and pearl-tubes saturated with a solution of sodium carbonate. The method of filling was as follows :—The swimmer was raised to A and the stopcock H closed. After the gas had flowed a short time through the ear-tubing, it was firmly clamped. The gas could now only escape through the side piece A, and thus the air still remaining in the upper portion of the main tube was rapidly expelled. The open end at O was then made air-tight and the stopcock H opened. The energy of the generation of the gas drove the water out of the tube back into the bottle, but always against a small counter-pressure, as I always took care that the surface

\* Corrected on page 264.

of the water in the bottle stood higher than the surface of that in the tube. In this way it was impossible for the air to penetrate into the tube, even though the apparatus had not been air-tight. Everything was, however, always perfectly air-tight. When the tube was full, the stopper at O and the clamp on the ear-tubing were removed, the tuning-fork bowed, and the positions of the maxima ascertained exactly as in the case of air. While the observations were being made, the gas apparatus remained in action, so that a slow steady stream of pure carbonic acid poured through the upper portion of the tube and overflowed its edges.

The observed half wave-length was corrected to  $0^{\circ}$  C. and 760 millim. in dry gas by means of a formula analogous to the one used for air.

Table showing the observed mean velocities in  $\text{CO}_2$ .

Internal diameter of the tube.	$c_1$ $n=256.$	$e_1$ $n=320.$	$g_1$ $n=384.$	$c_{II}$ $n=512.$	$c_{III}$ $n=1023\cdot25.$
millim. 28	metre. 255·38	metre. 255·73	metre. 255·86	metre. 256·05	metre. 256·37
17·1	254·53	254·96	255·24	255·36	255·78
9·35	252·58	253·03	253·41	253·69	254·49

By combining the results in the vertical columns in pairs as explained on page 254 for air, we find the following values for the velocity of sound in carbonic acid in unlimited space.

Tuning-fork.	Tubes I. and II.	Tubes I. and III.	Tubes II. and III.	Mean.
	millim.	millim.	millim.	millim.
$c_1$ .....	256·7	256·7	256·7	256·7
$e_1$ .....	256·8	257·1	257·2	257·03
$g_1$ .....	256·8	257·2	257·5	257·17
$c_{II}$ .....	257·0	257·2	257·2	257·13
$c_{III}$ .....	257·0	257·2	257·2	257·13
			Mean .....	257·03

For the purpose of comparing my results for air and carbonic acid with those of other observers, I have constructed

the following table, in which the values for carbonic acid are referred to those for air as unity.

	Dulong *.	Regnault †.	Wüllner ‡.	Kundt §.	Low.
Air .....	1	1	1	1	1
CO <sub>2</sub> .....	0.7856	0.8009	0.7812	0.7785	0.77750

To test further the validity of Kirchhoff's formula, I have, as before, calculated the products  $(a-v)2r$  and  $(a-v)\sqrt{n}$  for  $a=257.03$  metre. The results, taken vertically in the first table and horizontally in the second, should be constant.

TABLE I.

Values of  $(a-v)2r$ .

Tube.	$c_r$ .	$e_r$ .	$g_r$ .	$c_{ii}$ .	$c_{iii}$ .
I. ....	0.04620	0.03640	0.03273	0.02745	0.01848
II. ....	4275	3540	3061	2856	2137
III. ....	4161	3741	3385	3123	2374

TABLE II.

Values of  $(a-v)\sqrt{n}$ .

Tube.	$c_r$ .	$e_r$ .	$g_r$ .	$c_{ii}$ .	$c_{iii}$ .
I. ....	26.40	23.26	22.93	22.17	21.11
II. ....	39.99	37.03	35.09	37.79	39.98
III. ....	71.24	71.47	70.94	75.56	81.25

Here, again, the deviations from a constant mean are quite unimportant, and are evidently due to small errors of observation.

\* *Ann. de Chim. et de Phys.* tom. x. p. 41.

† Regnault, see footnotes, p. 249.

‡ *Lehrbuch der Physik*, iv. Aufl. 1, p. 804.

§ Kundt, see footnotes, p. 249.

The values of  $\gamma$ , the constant for friction and conduction of heat, are as follows:—

Tube.	$c_r$	$e_r$	$g_r$	$c_{ii}$	$c_{iii}$
I. ....	0.005099	0.004490	0.00424	0.004284	0.004078
II. ....	4718	4367	4137	4457	4706
III. ....	4592	4615	4575	4873	5240
Mean = 0.004577.					

The ratio of the specific heats, calculated in the same way as for air, I found to be 1.2883. Röntgen\* gives 1.3052 and Müller† 1.2653.

To recapitulate,—

1. Kirchhoff's formula for the determination of the velocity of sound in tubes holds good for carbonic acid as well as for air if the velocity in the free gas = 257.03 metre‡, and the constant for friction and conduction of heat = 0.004577.

(2) The ratio of the specific heats for carbonic acid is 1.2883 ‡.

### § 5. Hydrogen.

The remodelling of the apparatus for gases lighter than air caused much trouble. In its final form I simply inverted the whole apparatus as employed for carbonic acid. It was now in fact a siphon; the open end of the tube was below and the stopcock above. The few drops of water that trickled out I led aside with a tail of lamp-wick. The method of filling was the same as for carbonic acid, only here everything was inverted.

On account of the extraordinary tenuity of this gas, the wave-lengths are very great, and much longer tubes than before were necessary. I soon found that the energy of the vibrating mass of the gas was too small to set the membrane of the tympanum properly in vibration, and that exact readings of the maxima were unattainable.

The following readings were taken with tube II. and fork  $c_{ii}$  at a temperature of 15° C.:—

\* Pogg. Ann. cxlviii. p. 612 (1874).

† Wied. Ann. xviii. p. 116 (1883).

‡ Corrected on page 264.



$\frac{\lambda}{2}$ millim.	$v_0$ metre.
1185	1260·4
1120	1172·0
1175	1250·6
1160	1234·2
1150	1223·3
1145	1217·9
1220	1297·5

---

Mean 1236·5

Regnault gives 1200·77 and 1166·67, but these numbers are probably too small.

According to a few experiments which I made later with coal-gas, the form of the apparatus that was used for carbonic acid seems also suitable for gases lighter than air. In this case, however, the observer must operate as rapidly as possible.

### § 6. *Mixtures.*

I also applied the method with good success to mixtures of air and vapours. The form of the apparatus was the same as for air, only that in this case the bottle was filled with the evaporating liquid instead of with water.

I raised the liquid in the tube as far as the side-piece A, then let it slowly sink and remain standing for a time, which varied from a few seconds to two hours. The temperature for all the experiments was constant (17° C.). With tube II. and fork  $c_{III}$  I took six sets of readings given below. At the beginning of each set, one or two half wave-lengths come where only very little vapour was present. Then with increasing saturation the half wave-lengths gradually decrease, until in the immediate neighbourhood of the liquid they become constant.

### Experiments with Ethyl-ether Vapour.

	1.	2.	3.	4.	5.	6.
	Surface of ether below.					
$\frac{\lambda}{2}$ millim. = 160	153	—	156	153	159	
144	154	145	151	153	156	
130	143	130	132	132	132	
109	110	108	112	110	114	
108	110	114	112	112	112	
112	110	110	113	113	110	
109	109	109	110	110	110	
	Surface of ether above.					

The mean of the last six half wave-lengths in the immediate neighbourhood of the surface of the liquid is 109.5 millim.

The velocity of sound in air  $v$  is calculated by the formula

$$v^2 = \frac{B \cdot Q \cdot g}{\frac{\sigma}{\bar{k}}},$$

where  $B$  denotes the barometric height,  $Q$  the specific gravity of mercury,  $g$  the accelerating force of gravity,  $\sigma$  the density of air referred to water, and  $\bar{k}$  the ratio of the specific heats. The analogous formula, when vapour is present, is

$$\begin{aligned} v^2 &= \frac{B \cdot Q \cdot g}{\frac{\sigma}{\bar{k}} + \frac{\sigma_1}{\bar{k}_1}} \\ &= \frac{B \cdot Q \cdot g (1 + \alpha t)}{\frac{\sigma_0}{\bar{k}} \cdot \frac{p - S}{p_0} + \frac{\sigma_0}{\bar{k}_1} \cdot \frac{uS}{p_0}}, \end{aligned}$$

where  $u$  = density of the vapour compared with air, and  $\alpha$  = thermal coefficient of expansion of gases.

Or

$$\begin{aligned} v^2 &= \frac{p_0 \bar{k} (1 + \alpha t)}{\sigma_0 \left( 1 - \frac{S}{p} + \frac{\bar{k}}{\bar{k}_1} u \cdot \frac{S}{p} \right)} \\ &= \frac{p_0 \bar{k} (1 + \alpha t)}{\sigma_0} \cdot \frac{1}{1 + \left( \frac{\bar{k}}{\bar{k}_1} u - 1 \right) \frac{S}{p}} \\ &= \frac{B_0 \cdot Q_0 \cdot g \cdot \bar{k}}{\sigma_0} \cdot \frac{1 + \alpha t}{1 + \left( \frac{\bar{k}}{\bar{k}_1} u - 1 \right) \frac{S_{\text{millim.}}}{B_{\text{millim.}}}}; \end{aligned}$$

or

$$v = v_0 \sqrt{\frac{1 + \alpha t}{1 + \left( \frac{\bar{k}}{\bar{k}_1} u - 1 \right) \frac{S}{B}}}$$

In further explanation of the above I add

	Air.	Ether vapour.
Density .....	$\sigma = \frac{1}{773}$	$\sigma_1 = u\sigma = 2.60 \sigma$
Sp. heat const. pressure	$\bar{k}$	$\bar{k}_1$
Sp. heat const. volume		
Partial pressure .....	$p - S$	$S$

Pressure  $p = B \cdot Q \cdot g$ ,

$$p_0 = B_0 \cdot Q_0 \cdot g,$$

$$= 0.760 \times 13.596 \times 9.810 \text{ metre.}$$

If  $k_1$  be the unknown, then

$$k_1 = \frac{ku}{\left\{ \frac{v_0^2}{v^2} (1 + \alpha t) - 1 \right\} \frac{B}{S} + 1}.$$

By substituting

$$k = 1.3968,$$

$$\alpha = 0.003665,$$

$$u = 2.600,$$

$$t = 17^\circ \text{C.},$$

$$v_0 = 330.88 \text{ metre,}$$

$$B = 0.750 \text{ metre,}$$

$$v = 2 \times 1023.25 \times 0.1095 \text{ metre,}$$

$$S = 0.38528 \text{ metre,}$$

we get as ratio of the specific heats of ethyl-ether

$$k = 1.0202.$$

Jaeger\* found 1.097 (at  $20^\circ$ ) and Müller† 1.0288 (between  $45^\circ.4$  and  $22^\circ.5$ ).

A phenomenon, similar to the one observed in a mixture of air and vapour, I found also in a mixture of air and carbonic acid.

In the manner already described I filled the tube half full with carbonic acid, then turned the gas off and let the water sink. The upper portion of the tube was thus filled with air and the lower with carbonic acid. With fork  $c_{III}$  and tube II. I found the following readings:—

Surface of the water below.

165	165	} air.
165	165	

150	140	} carbonic acid.
135	135	
130	130	
130	130	

Surface of the water above.

In both columns the two first half wave-lengths agree with those previously found for pure air, the two last with those for pure carbonic acid. This is a simple method of ascertaining with fair exactness the relative velocities of sound in air and carbonic acid or other suitable gases.

\* Wied. *Ann.* xxxvi. p. 209 (1889).

† Wied. *Ann.* xviii. p. 116 (1883).

## § 7.

After my experiments were finished I had some doubt as to whether the vibration-frequency of  $c_1$  was exactly 256. I decided the point by means of an electric registration method. A small, thin, pointed piece of platinum-plate was attached to the end of one of the prongs of the fork, and the vibration-curves were traced on a metal cylinder coated with blackened paper. A weak induction-current, with mercury contact with the seconds-pendulum of a clock of known daily error, was generated and conducted by the platinum point to the blackened paper. The number of waves between the marks of the sparks, taken two and two, gave the double vibration-frequency of the fork. As a result I found that  $c_1$  made 256·23 vibrations per second. This necessitated small corrections in my results, which are shown below.

## Velocity of Sound.

	Uncorrected.	Corrected.	Regnault *.
Air.....	330·582 m.	330·88 m.	330·7 m.
Carbonic Acid ...	257·03 m.	257·23 m.	259·57 m.
Hydrogen .....	1236 5 m.	1237·6 m.	1200·77 & 1166·67 m.
Ether Vapour ...	175·77 m.	175·93 m.	178 8 m.†

## Corresponding corrected Ratios of the Specific Heats.

	Low.	Röntgen ‡.	P. A. Müller §.
Air.....	1·3968	1·4053	1 4062
Carbonic Acid ...	1·2914	1·3052	1·2653
Hydrogen .....	1·3604	1·3852	.....
Ether Vapour ...	1·0244	.....	1·0288 (at 22°) 1·094 †

\* *Mém. de l'Inst.* xxxvii. p. 133; *Compt. Rend.* lxvi. p. 219 (1868).

† Jaeger, *Wied. Ann.* xxxvi. p. 209 (1889).

‡ Pogg. *Ann.* cxlviii. p. 603 (1873).

§ *Wied. Ann.* xviii. p. 116 (1880).

The experiments with hydrogen can only be regarded as approximately correct.

My results for the velocity of sound in air and carbonic acid in glass tubes of different diameters are in full agreement with Kirchhoff's theoretical formula founded upon the consideration of the friction and the conduction of heat of gases.

The velocity of sound in free space for air and carbonic acid is, according to my results, invariable for tones of different pitch and intensity.

It is my pleasant duty to express here to Professor Quinke my heartiest thanks for his kind support and instructive counsel during the prosecution of the above inquiry.

The Physical Institute, Heidelberg,  
January 1894.

### XXIX. *The Hatchet Planimeter.* By F. W. HILL\*.

THE hatchet planimeter consists essentially of a tracing-point and a convex chisel-edge rigidly connected, the point and the edge being in the same plane. When the point is moved along any line, the edge describes a curve of pursuit.

The object of this paper is to investigate how the instrument may be used to determine areas.

Let the tracer start from a point O inside the area, move along any line to the perimeter, then round the perimeter and back along the same line to O; the solution of the problem consists in finding an expression for the angle AOB between the initial and final positions OA, OB of the line joining the tracing-point and chisel-edge.

All attempts to express the area of the curve in terms of this angle proved futile except in a few special cases, such as the circle and square; but the magnitude of the angle may be found in the form of an infinite series, the most important term of which is a multiple of the area. The complexity of the result would seem to show that no simple geometrical explanation is possible.

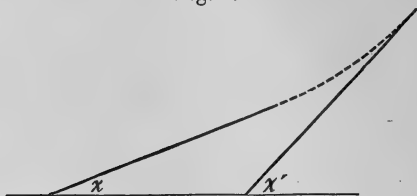
Let the tracer move a distance  $r$  along a straight line (fig. 1); then, if  $\chi$ ,  $\chi'$  be the initial and final inclinations of the rod to the line,  $c$  the length of the rod, it is easily proved that

$$\tan \frac{\chi'}{2} = e^{\frac{r}{c}} \tan \frac{\chi}{2}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

\* Communicated by the Physical Society: read June 22, 1894.  
*Phil. Mag.* S. 5. Vol. 38. No. 232. Sept. 1894. T

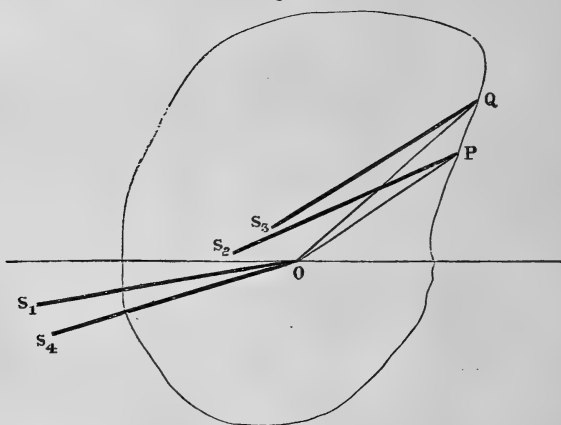
Let the area of the curve be divided into infinitesimal triangles having their vertices at a point O inside the curve,

Fig. 1.



and for their bases elements of the perimeter, the problem is best attacked by making the tracer move round each of these triangles in turn, travelling along every radius-vector twice, in opposite directions. Taking any triangle OPQ (fig. 2),

Fig. 2.



let  $\theta, \theta + d\theta$  be the inclinations of OP, OQ to a fixed line OX;  $\phi, \phi', \phi' + d\phi', \phi + d\phi$ , the inclinations of the rod to the fixed line in the positions  $S_1O, S_2P, S_3Q, S_4O$  respectively;  $r, r + dr$  the lengths of OP, OQ.

Then by (1)

$$\tan \frac{\theta - \phi'}{2} = e^{-\frac{r}{c}} \tan \frac{\theta - \phi}{2} \quad \dots \quad (2)$$

$$\text{and} \quad \tan \frac{\theta + d\theta - \phi' - d\phi'}{2} = e^{-\frac{r+dr}{c}} \tan \frac{\theta + d\theta - \phi - d\phi}{2}$$

for the motions from O to P, and from Q to O; hence

$$\frac{d\theta - d\phi'}{\sin(\theta - \phi')} = -\frac{dr}{c} + \frac{d\theta - d\phi}{\sin(\theta - \phi)} \quad \dots \quad (3)$$

Also from (1) by differentiating,

$$\frac{d\chi}{\sin \chi} = \frac{dr}{c}.$$

Now if  $\psi$  be the angle between OP and the tangent PQ, the inclinations of the rod to PQ are  $\psi - \theta + \phi'$  at P, and  $\psi - \theta + \phi' + d\phi'$  at Q, and the length PQ is  $ds$ ;

therefore 
$$\frac{d\phi'}{\sin (\psi - \theta + \phi')} = \frac{ds}{c},$$

or 
$$cd\phi' = \{ \sin \psi \cos (\theta - \phi') - \cos \psi \sin (\theta - \phi') \} ds$$
  

$$= rd\theta \cos (\theta - \phi') + dr \sin (\theta - \phi').$$

Substituting this value of  $d\phi'$  in (3),

$$\frac{cd\theta - rd\theta \cos (\theta - \phi')}{\sin (\theta - \phi')} - dr = -dr + \frac{c(d\theta - d\phi)}{\sin (\theta - \phi)},$$

or 
$$\frac{d\theta - d\phi}{\sin (\theta - \phi)} = \frac{d\theta}{2} \left( 1 - \frac{r}{c} \right) \cot \frac{\theta - \phi'}{2} + \frac{d\theta}{2} \left( 1 + \frac{r}{c} \right) \tan \frac{\theta - \phi'}{2}$$
  

$$= \frac{d\theta}{2} \left( 1 - \frac{r}{c} \right) e^{\frac{r}{c}} \cot \frac{\theta - \phi}{2} + \frac{d\theta}{2} \left( 1 + \frac{r}{c} \right) e^{-\frac{r}{c}} \tan \frac{\theta - \phi}{2}$$

by (2);

$$\therefore d\theta - d\phi = \left[ \left( 1 - \frac{r}{c} \right) e^{\frac{r}{c}} \cos^2 \frac{\theta - \phi}{2} + \left( 1 + \frac{r}{c} \right) e^{-\frac{r}{c}} \sin^2 \frac{\theta - \phi}{2} \right] d\theta$$
  

$$= \frac{1}{2} \left[ \left( 1 - \frac{r}{c} \right) e^{\frac{r}{c}} + \left( 1 + \frac{r}{c} \right) e^{-\frac{r}{c}} \right] d\theta$$
  

$$- \frac{1}{2} \left[ \left( 1 + \frac{r}{c} \right) e^{-\frac{r}{c}} - \left( 1 - \frac{r}{c} \right) e^{\frac{r}{c}} \right] d\theta \cos (\theta - \phi)$$
  

$$= \left( 1 - \frac{r^2}{2c^2} - \frac{r^4}{8c^4} - \frac{r^6}{144c^6} - \dots \right) d\theta$$
  

$$- \left( \frac{r^3}{3c^3} + \frac{r^5}{30c^5} + \dots \right) \cos (\theta - \phi) d\theta.$$

Or

$$c^2 d\phi = \frac{r^2 d\theta}{2} + \frac{r^4}{8c^2} d\theta + \frac{r^6}{144c^4} d\theta$$
  

$$+ \left( \frac{r^3}{3c} + \frac{r^5}{30c^3} + \dots \right) d\theta \cos (\theta - \phi). \quad \dots (4)$$

This equation gives the change in the direction of the rod when the tracing-point has moved round an elementary

triangle, and integrating round the curve there results, for the angle between the initial and final positions of the rod, the expression

$$c^2\Phi = A + \frac{1}{8c^2} \int r^4 d\theta + \frac{1}{144c^4} \int r^6 d\theta + \dots \\ + \int \left( \frac{r^3}{3c} + \frac{r^5}{30c^3} + \dots \right) \cos(\theta - \phi) d\theta,$$

where  $A$  is the area of the curve, and the integrations extend from  $\theta=0$  to  $\theta=2\pi$ . Thus if the greatest breadth of the curve is less than the length of the planimeter, the most important term in the expression is  $A$ , and it remains to estimate the effect of the other terms.

First, considering those terms which depend only on the position of  $O$ ,

$$\frac{1}{8c^2} \int r^4 d\theta = \frac{Ak^2}{2c^2},$$

where  $Ak^2$  is the moment of inertia of the area about the polar axis through  $O$ . This term is therefore least when  $O$  is the mass-centre of the area.

$$\frac{1}{144c^4} \int r^6 d\theta \text{ is less than } \frac{2A}{144} \left( \frac{a}{c} \right)^4,$$

where  $a$  is the greatest radius-vector from  $O$ , and, if  $\frac{a}{c}$  is as great as  $\frac{1}{8}$ , is less than one per cent. of the area.

Of the terms depending on  $\phi$  the most important is

$$\frac{1}{3c} \int r^3 \cos(\theta - \phi) d\theta.$$

In these small terms the value of  $c^2\phi$  at any point may be taken to be the area of that part of the curve already described by the tracing-point, and the terms can be evaluated when the equation of the curve is known. If, however, the area of the curve is less than that of a square of side  $c$ , so that the greatest value of  $\phi$  is less than 1, it is easy to approximate.

$$\frac{1}{3c} \int r^3 \cos(\theta - \phi) d\phi = \frac{1}{3c} \int r^3 \cos \theta d\theta + \frac{1}{3c} \int r^3 \phi \sin \theta d\theta \\ - \frac{1}{6c} \int r^3 \phi^2 \cos \theta d\theta + \dots$$

Now, the axis of  $x$  being the initial position of the rod,



$$\frac{1}{3c} \int r^3 \cos \theta d\theta = \frac{1}{c} \int x dA = \frac{A\bar{x}}{c},$$

where  $\bar{x}$  is the abscissa of the mass-centre of the area. The other terms are multiplied by  $\left(\frac{a}{c}\right)^3$ , and being integrals of oscillating quantities are very small.

Thus

$$c^2\Phi = A + \frac{Ak^2}{2c^2} + \frac{A\bar{x}}{c} + \frac{P}{c^3},$$

where P is very small.

If O is the mass-centre of the curve  $k^2$  is a minimum and  $\bar{x}=0$ . In this case

$$c^2\Phi = A\left(1 + \frac{\rho^2}{2c^2}\right)$$

very nearly, where  $A\rho^2$  is the moment of inertia about the polar axis at the mass-centre.

If O is not near the mass-centre, let the tracing-point be moved again round the perimeter, following the same path as before, but with the initial direction of the instrument exactly reversed; the effect of this is to change the sign of  $c$  and to give

$$c^2\Phi' = A + \frac{Ak^2}{2c^2} - \frac{A\bar{x}}{c} - \frac{P}{c^3};$$

hence

$$\frac{c^2}{2} (\Phi + \Phi') = A + \frac{Ak^2}{2c^2}.$$

$c\Phi$  being the distance between two indentations may perhaps be measured to within  $\frac{1}{100}$  inch, so that there will be an error in  $c^2\Phi$  of at least  $\frac{1}{20}$  sq. inch, if  $c$  is 10 inches; if, therefore,  $\frac{Ak^2}{2c^2}$  is less than  $\frac{1}{20}$  sq. inch, it may be neglected.

Of curves with the same greatest breadth, the circle has the greatest area, and  $\frac{Ak^2}{2c^2}$  is less than  $\frac{1}{20}$  sq. inch for a circle of radius  $1\frac{1}{2}$  inches.

Finally, then, if O be near the mass centre, and the greatest breadth be less than 3 inches, the formula  $c^2\Phi = A$  will give a result as accurate as the nature of the instrument will allow; for greater areas the value of  $\frac{Ak^2}{2c^2}$  must be estimated and taken into account. Also it is easily verified that if  $\Phi$  is less than  $\frac{1}{13}$ , or the area less than 23 sq. inches, it is sufficient to measure the chord of the arc  $c\Phi$  instead of the arc.

XXX. *Magnetic Shielding by a Hollow Iron Cylinder. Simplest Case.* By JOHN PERRY, F.R.S.\*

**I** CONSIDER going and return electric conductors each at a distance  $a$  from the axis in a diametral plane of the hollow cylinder, the current in each being  $C$ .

As to the inducing magnetic potential, all over one half of the cylindric surface of radius  $a$  the potential is constant,  $\pi C$ , and all over the other half it is constant, being  $-\pi C$ . At a point  $P$  whose distance from the axis is  $r$ , the angle made by the axial plane through  $P$  and the plane through the conductors being  $\theta$ , it is evident that  $V$ , the inducing potential, is

$$V = 4C \left( \frac{a}{r} \sin \theta + \frac{1}{3} \frac{a^3}{r^3} \sin 3\theta + \frac{1}{5} \frac{a^5}{r^5} \sin 5\theta + \&c. \right),$$

as this becomes  $+\pi C$  or  $-\pi C$  where  $r=a$ , and also satisfies  $\nabla^2 V = 0$ .

Let the coefficient of  $\sin n\theta$  in  $V$  be denoted by  $Ar^{-n}$ ; let the corresponding coefficients be  $A_1 r^n + Ar^{-n}$  for the total (induced plus inducing) potential inside the tube;  $A_2 r^n + B_2 r^{-n}$  total in the iron and  $B_3 r^{-n}$  in outside space. Let the inside and outside radii of the iron cylinder be  $a_1$  and  $a_2$ . Then, on stating the equality of the potentials just inside and just outside the two surfaces, and also that the normal induction is the same on both sides, we have four equations, which enable the coefficients  $A_1$ ,  $A_2$ ,  $B_2$ , and  $B_3$  to be calculated. The two important ones are

$$B_3 = 4\mu A / \{ (\mu + 1)^2 - e(\mu - 1)^2 \},$$

where  $e$  stands for  $a_1^{2n}/a_2^{2n}$ ,

$$\text{and} \quad A_1 = -A\rho(1-e)/a_1^{2n}(\rho^2 - e),$$

where  $\rho = (\mu + 1)(\mu - 1)$ .

If we take  $a_2 = a_1 + t$ , and  $t$  is small, since  $\mu$  is large in iron, we have approximately

$$B_3 = A \left/ \left( 1 + \frac{1}{2} \mu n \frac{t}{a_1} \right) \right.$$

The higher terms are unimportant. Taking the first: the unshielded potential was  $4Car^{-1} \sin \theta$ , and it is converted by shielding into  $4Ca \sin \theta / r \{ 1 + \frac{1}{2} \mu t / a_1 \}$ .

Thus, taking  $\mu = 1200$ ,  $a_1 = 150$  cm.,  $t = 5$  cm., the first and most important term is reduced to the 1/21st part of its

\* Communicated by the Physical Society: read June 22, 1894.

unshielded value. The other terms are reduced to  $1/61\text{st}$ ,  $1/101\text{st}$ ,  $1/141\text{st}$ , &c., parts of their unshielded values.

In this case the potential inside is very little less than when there was no iron,  $A_1$  being  $-A/a_1^{2n}$  for all values of  $t$  until  $t$  is small; of course  $A_1$  is 0 when  $t$  is 0.

It is easy to extend the reasoning to several enveloping cylinders of iron, or to the case of any distribution of inducing potential which does not vary in a direction parallel to the axis.

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XXXI. *The Clark Cell when Producing a Current.* By S. SKINNER, M.A., Lecturer at Clare College, and Demonstrator at the Cavendish Laboratory, Cambridge\*.

§ 1. *Introduction.*

THE electromotive force of the Clark cell when not producing any current has been frequently determined, and has been found to be of so constant a value that it is now used as a standard. These values of E.M.F. are for the cell when its poles are not united by a conductor. In the following account is given of a series of experiments made on cell when producing currents, with the view of ascertaining, (1) how far the total electromotive force round the circuit differs from that of the open cell, and (2) how this new value for the E.M.F. changes when the current is maintained. If these quantities can be accurately measured, it follows that a cell might be used for producing currents of known value. Some experiments have been made on subject (2) by Threlfall and Pollock (Phil. Mag. November 1889), and their results are compared with mine in Sect. 8.

§ 2. *The Cells.*

The experiments were made on three cells, all much larger than the ordinary Board-of-Trade pattern of Clark cell.

Cell B, made July 1891, is the cell no. 90 described on p. 558 of the paper by Mr. Glazebrook and the author, Phil. Trans. 1892, A. The area of its exposed zinc surface is approximately 14.4 square centimetres.

Cell L, made November 1892, is a much larger cell fitted up in a cylindrical jar 22 centim. high and 13 centim. in diameter. The zinc plate exposes an area of about 95 square centimetres.

Cell N, made July 1893, is intermediate in size and exposes about 29 square centimetres of zinc surface.

\* Communicated by the Physical Society: read June 22, 1894.

In all three cells the zinc plate, a piece of common zinc sheet, is placed horizontally, and they have the same E.M.F. within 2 parts in 5000.

### § 3. *The Effect of Uniting the Poles of a Cell.*

Let a cell of electromotive force  $E$  and internal resistance  $R$  have its poles joined by a wire of resistance  $r$ ; then, providing  $R$  and  $r$  are constant, and there is no polarization, the potential-difference between the poles will be  $\frac{rE}{R+r}$ . If, however, there is polarization, then this potential-difference will be  $\frac{re}{R+r}$ , where  $e$  is the value of the electromotive force required to produce the observed current.

The value of  $-(E-e)$  is the electromotive force of polarization.

In the large Clark cells described above  $E$  and  $e$  are nearly equal when the current is not larger than .01 ampere; this small difference is the subject of the following measurements. To obtain it, it is clearly necessary to find the value of the potential-difference  $\frac{re}{R+r}$ , and of the resistances  $R$  and  $r$ .

The measurements for  $R$  are contained in Sect. 4;  $r$  consisted of thick wire coils or of a special wire resistance immersed in a large tank of paraffin oil; and the measurements of the potential-differences are contained in Sect. 6.

We shall now give an illustration, taken from an actual experiment, of what happens when the poles of a cell are united. On July 25th the cell L had an electromotive force, with its poles open, represented by 5009 on the compensator. The poles were then joined by a resistance of 1000 legal ohms, and their potential-difference, taken as quickly as possible, was then rather more than 4983 and rather less than 4984. Then a resistance of 500 legal ohms was substituted for the 1000; the potential-difference fell to 4959. Next, with 200 legal ohms the potential-difference was 4885. Lastly, the poles were opened, and the electromotive force of the cell was found to be 5009.

It is seen from these numbers that the cell recovered its electromotive force entirely after the various operations, and this is a typical instance of the behaviour of the cells. It should be mentioned here that these tests, as well as tests on two other cells, were made in the interval between the two sets of resistance observations recorded in the column of the table § 4, headed "July 25th, Before—After."

#### § 4. *Measurement of the Internal Resistance of the Cells.*

The important determination of the resistance of the cells was made by the method of Opposition, and by the use of an Alternating Current. By opposing any two of the cells, the resulting electromotive force was so small that, making them an arm in a Wheatstone's arrangement, there was no deflexion in the bridge-galvanometer. The bridge was fed with an alternating intermittent current by means of the commutator used by Mr. T. C. Fitzpatrick in his electrolytic measurements, B. A. Report, 1886, p. 328.

In this method the commutator is arranged to supply the currents in the galvanometer-circuit always in the same direction, so that an ordinary sensitive mirror-galvanometer can be used. The drum of the commutator has on each circular face eight insulated sectors of brass, those on one side being larger than those on the other. The larger sectors are connected by brushes to the battery-circuit, and the smaller to the galvanometer-circuit. They are arranged so that the battery connexion is always closed before that of the galvanometer, and is always broken after that of the galvanometer. A more complete description of the commutator, which works excellently, will be found in the paper already mentioned. Two or three Leclanché cells were used as the battery.

The method of connecting two cells together so as to have small resulting electromotive force is particularly applicable in the case of Clark cells, for they may be obtained of nearly equal electromotive force. In the case of the cells we are discussing, as mentioned in § 2, the greatest difference was never more than 2 in 5000.

The errors to which this method of measuring battery-resistance is liable are two: first, from self-induction, and second, from polarization at the electrodes. The only conductor containing self-induction of any magnitude is the galvanometer-coil, and as the method is a zero method this does not matter. The second error is eliminated by using an alternating current. However, following Fitzpatrick's method, tests were specially made for polarization by varying the ratio of the arms and by varying the speed of the commutator. For instance, on one occasion the resistance was between 11.0 and 11.1 with the usual speed for working; when the speed was more than doubled, the resistance retained the same value.

The three cells were measured in pairs, and the results in legal ohms are given in the following table, where C is the resistance of the connecting wires.

The words "Before," "After," refer to the relation of these measurements to those recorded in § 6.

Cells.	July 20th. 16°·8.	July 23rd. 18°.	July 24th. 17°·8.	July 25th. 17°·8.	
	<i>After.</i>	<i>Before.</i>		<i>Before.</i>	<i>After.</i>
N+B+C .....	13·20	12·8	13·1	13·25	13·11
L+B+C .....	11·69	10·8	11·05	11·15	11·10
N+L+C .....	11·04	10·7	10·9	10·98	10·90
C .....	0·93	0·93			
From which are calculated the following values of resistance :—					
L .....	4·30	3·88	3·96	3·97	3·98
N .....	5·81	5·88	6·01	6·07	5·99
B .....	6·46	5·99	6·16	6·25	6·19

The temperatures are those of the water-bath in which the cells stood ; the cells were not moved during the whole of the measurements. It will be noticed that the resistance of the cells is lower at high than at low temperature. This agrees with the fact that electrolytes decrease in resistance with increase of temperature.

#### § 5. *The Resistances, and Apparatus for Comparison of Electromotive Forces.*

The compensating apparatus was the same as that described in § 8 of the paper by Mr. Glazebrook and the author already quoted. However, in the place of the Leclanché cells there described to produce the main current, I used one or two large Clark cells. The reason for this change arose from the irregular behaviour of the Leclanché cells, when changes were made in the amount of current taken from them. The results of eleven series of observations were rendered useless on this account. When only one Clark was used in the main circuit, the standard cell for reference was a Helmholtz mercurous-chloride cell, § 7. When two Clark cells were used, the standard was some other Clark cell which was kept at rest.

The circuits, through which the currents from the cells under test were taken, consisted of thick wire coils from a legal ohm resistance-box for the values 1000, 500, 200 legal ohms, and of a german-silver wire of 147 legal ohms wound on an ebonite frame, which was placed in a tank of paraffin oil. This german-silver wire was always used when the current was maintained for any length of time, as from its construction its temperature could be very accurately observed.

§ 6. *Determination of the Electromotive Force of Polarization.*

By means of the method described in § 5 the results in the following table were obtained. The units of electromotive force are approximately  $\frac{1.4}{5000}$  volts.

Cell and Date.	E.M.F. of cell open = E.	Potential-difference for the cell producing approximately :—			
		·0014 ampere $r=1000$ legal ohms.	·0028 ampere $r=500$ legal ohms.	·007 ampere $r=200$ legal ohms.	·01 ampere $r=147$ legal ohms.
L. July 20...	5010	.....	.....	.....	4837
L. „ 23...	5009	4985	4961.5	4890.5	
L. „ 25...	5009	4983.5	4959	4885	
N. „ 25...	5007.5	4959.5	4912		
B. „ 25...	5007	4971.5	4938.5	4841	

The simplest way to examine these results will be to calculate the electromotive force required to produce the observed current, when the cells are producing currents of different values. Using, then, the equation

$$e = \frac{R + r}{r} \times \text{potential-difference,}$$

with values of R from § 4 and of  $r$  from § 5, we have the following values of  $e$  :—

	E.	$e$ for ·0014 ampere.	$e$ for ·0028 ampere.	$e$ for ·007 ampere.	$e$ for ·01 ampere.
L .....	5010	.....	.....	.....	4981
L .....	5009	5005	5001	4988	
L .....	5009	5005	4999	4983	
N .....	5007.5	4989	4971		
B .....	5007	5003	5000	4990	

From which we obtain the values for  $E - e$ , the electromotive force of polarization being  $-(E - e)$ .

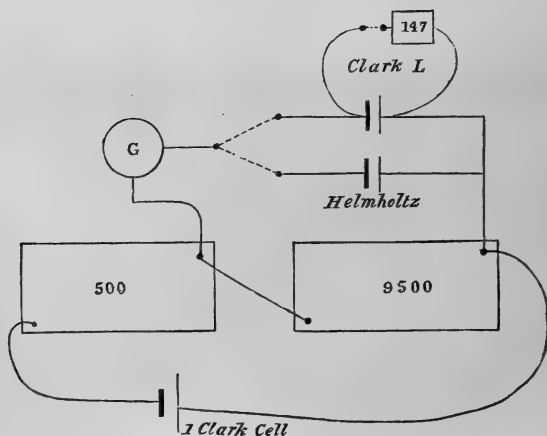
	$E - e$ for '0014 ampere.	$E - e$ for '0028 ampere.	$E - e$ for '007 ampere.	$E - e$ for '01 ampere.
L .....	.....	.....	.....	29
L .....	4	8	21	
L .....	4	10	26	
N .....	18.5	36.5		
B .....	4	7	17	

It will be observed that for a given cell the electromotive force of polarization is directly proportional to the current-density.

§ 7. *Effect with Time, the Current being maintained.*

The experiments to be described in this section show how the potential-difference varies when the cell is allowed to produce a current for some time. For these experiments the standard of reference was a set of Helmholtz cells described in the paper quoted above, p. 618 ; they were immersed in a tank of paraffin oil. On January 17th they were submitted to a very rigorous test for constancy, extending over four hours, a Clark cell being the standard. It is not necessary to say anything further about them.

Fig. 1.



The arrangement used in the experiments is illustrated in the accompanying diagram (fig. 1), which clearly explains itself.



A single Clark cell was used in the main circuit for the reason that it is so much more steady than the usual two Leclanché cells, *vide* § 8. The complete results of a single experiment are given in the following table :—

Time.		E.M.F.	Temperature. Oil.	Temperature. Water.
h	m			
11	14	Helmholtz 6890+	13 <sup>0</sup>	12 <sup>0</sup>
12	15	" 6891—	13	12.1
2	27	" 6891+	13.2	12.3
2	33	Clark L through 147 L. ohms.		
2	36	Clark L 9447+		
2	37	" 9447+		
2	38.5	" 9447+		
2	49	" 9447		
2	59	" 9446+		
3	5.5	" 9446		
3	13	" 9446—		
3	20	" 9445+		
3	29	" 9445—		12.4
3	33	Clark off		
3	35	Helmholtz 6891+	13.3	
4	4	" 6891+	13.4	12.5

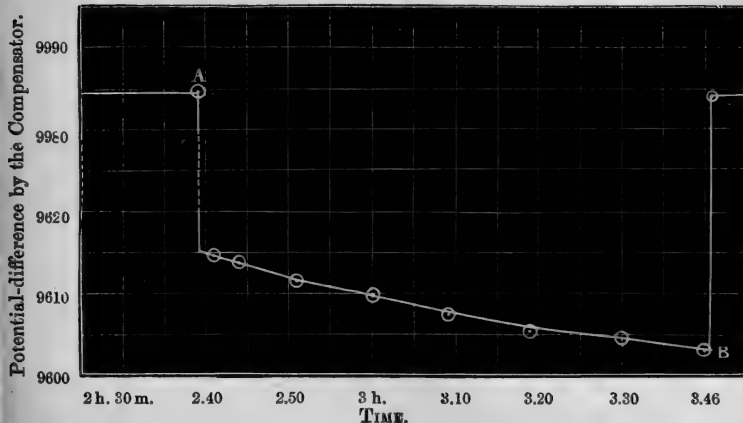
$$\text{Unit E.M.F.} = \frac{\text{E.M.F. Clark}}{10,000}$$

Another set of observations is given in the accompanying diagram (fig. 2).

Fig. 2.

Jan. 16th, 1893. Temperature 12°.—At A, the Clark cell L was short-circuited by 147 ohms. At B, the circuit was broken.

$$\text{Unit of E.M.F.} = \frac{\text{Clark}}{10,000}$$



The four experiments made by this method gave an average

fall of 7 units in the hour, and from the table § 6 we have the polarization on immediately making contact equal to 29 units  $\left(\frac{\text{Clark}}{5000}\right)$ , or 58 of our present units.

The polarization, or  $-(E-e)$ , for a current-density of  $\cdot 01$  ampere  $\frac{100 \text{ centim.}^2}{100 \text{ centim.}^2}$  for cell L may at any time be expressed approximately by

$$-(58 + 7t),$$

where  $t$  is the time in hours, and the unit of E.M.F. is  $\frac{\text{Clark}}{10,000}$ . Expressed in volts this is

$$-(\cdot 00834 + \cdot 001 t).$$

It is deduced from experiments on cell L, and only indicates the general order of magnitude of the effect with the other cells.

### § 8. Conclusion.

Throughout the calculations it has been assumed that the total electromotive force round the circuit is equal to that of the cell at rest; and therefore that the electromotive force overcoming polarization can be obtained by subtracting from the electromotive force of the cells at rest the observed current. With the exception of small Peltier effects, I know of nothing against this assumption.

The results of the experiments are :—

- (a) The electromotive force of polarization varies directly with the current-density in a particular cell.
- (b) The electromotive force of polarization slowly increases when the current is maintained.

From the magnitudes of the quantities found in these experiments, it follows that small currents of approximately known value can be obtained by the use of large Clark cells of small internal resistance, which may be neglected in comparison with the large external resistance. The experiments show that the large cell L when producing  $\cdot 01$  ampere was not at all disturbed. This corresponds to a current-density  $\cdot 01$  ampere

$\frac{95 \text{ (centim.)}^2}{10,000}$ . Now in a Board-of-Trade pattern Clark cell there is generally an exposed area of zinc equal to  $2 \text{ (centim.)}^2$ , and as the current taken is never greater than  $\frac{1.43}{10,000}$ , a 10,000 ohm coil being used in series with it, it follows that the current-density with this value of current is very

much below that which has been found to be safe in these experiments.

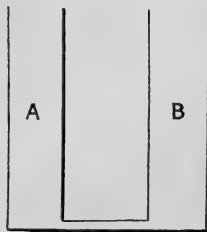
In the experiments of Threlfall the sign of the term depending on time was found to be negative. In some of my earlier experiments it appeared to be negative, but this was traced to irregularity in the working of the compensator ; and the effect has always been positive since the Clark cells have been used in the place of Leclanché, *vide* § 5.

XXXII. *On a Relation between the Surface-Tension and Osmotic Pressure of Solutions.* By B. MOORE, M.A., Exhibition Scholar, Queen's College, Belfast\*.

AT present the cause of osmotic pressure in solutions is unknown, although the laws regulating it and connecting it with the kindred solution phenomena, viz. the lowering of the freezing-point and of the vapour-pressure, have been well worked out within the last few years.

This paper is an attempt to show that it may be produced by difference in surface-tension acting along the exceedingly fine capillary openings of almost molecular dimensions which place the solution in connexion with its solvent in the pores of the semipermeable wall which separates them.

If two liquids which mix and have a different surface-tension be placed each in one of two wide tubes communicating beneath by a capillary, as shown in the figure, there is a surface over which capillary action will take place, between each liquid and the wall of the tube containing it. Suppose that the surface-tension of the liquid contained in A is the greater, and that the end of the capillary next A is filled with the pure liquid contained in A, and the end next B with the pure liquid contained in B, while between these two points there is a mixture of the two liquids. Then if  $T_1$  be the surface-tension of the liquid in A, and  $T_2$  that of the liquid in B, the tension along the walls of the capillary will diminish from  $T_1$  at the end next A to  $T_2$  at the end next B ; and the skin of liquid forming the surface of contact with the walls of the tube will be urged from B towards A by a force of  $(T_1 - T_2)2\pi r$ , where  $r$  is the radius of the capillary tube.



\* Communicated by Prof. Fitzgerald.

It might be supposed that the action of this force would cause a rise of level in the tube A. And so it would if the whole cross-section of the capillary were within the range of capillary action; but in a capillary tube, even as fine as one can draw it out, the greater part of the section is still outside the radius of capillary action, and as soon as any difference in pressure is caused by the action of surface-tension, it is effaced by a back flow along the central part of the capillary from A towards B.

However, under the circumstances in which osmotic pressure becomes evident, it is extremely probable that the diameters of the capillaries placing solution and solvent in communication are so exceedingly small that the whole of their cross-section is well within this radius of capillary action. That this is so appears to be proven, not only by the usual mode of formation of such semipermeable walls by causing a precipitate in a finely divided condition in pores already minute, so that the two fluids are only in communication by minute passages between the molecules of this precipitate which must most probably be of molecular dimensions, but also by a simple calculation based on the assumption that osmotic pressure is due to difference in surface-tension acting as above described.

This calculation leads to an interesting value for the dimensions of the pores and may be stated as follows:—Let  $T$  be the difference between the surface-tension of a solution and that of the pure solvent,  $P$  the osmotic pressure in this solution, supposed to be due to the action of this difference in surface-tension, and  $r$  the radius of a capillary opening placing the solution and the solvent in communication. Then, for a position of equilibrium, the difference in surface-tension acting on the perimeter of the capillary must balance the osmotic pressure acting on its cross-section, and we therefore conclude that the equation  $2\pi rT = \pi r^2P$ , or  $r = \frac{2T}{P}$ , must hold good.

From this equation, the necessary value which  $r$  must have, to account for osmotic pressure in the manner suggested, can easily be calculated.

Rother\* gives for the surface-tension of a solution of sodium chloride in water the equation  $\alpha = 7.357 + 0.1566y$ , where  $\alpha$  is the surface-tension in milligrams per millimetre, 7.357 the surface-tension of water in the same units, and  $y$  the number of gram-equivalents of the substance dissolved in 100 equivalents of water, that is in 900 grams. Converting

\* Wied. *Ann.* xvii. p. 353 (1882).

the equation into a more convenient system of units, it becomes  $T = 72.17 + 1.382n$ , where  $T$  is the surface-tension in dynes per centimetre, 72.17 the surface-tension of water expressed in the same units, and  $n$  the number of gram-molecules dissolved per litre.

Taking  $n$  equal to 1, the equation gives for the difference in surface-tension between a normal solution of sodium chloride and pure water, a value of 1.382 dynes per centimetre.

It is also easy to calculate approximately the osmotic pressure in a normal solution of the same salt, the amount of its dissociation at this concentration being known from Kohlrausch's conductivity determinations. Such a calculation gives for the osmotic pressure in such a solution the value of  $21 \times 10^6$  dynes per square centimetre. Substituting these values in the equation  $r = \frac{2T}{P}$ , the value obtained for the radius of the capillary opening is  $r = 18 \times 10^{-7}$  centimetres.

Now the limits of the radius of capillary action have been determined by various observers and by different methods, and are found to be much greater than this. Thus Plateau's determinations give, for  $l$ , the radius of capillary attraction,

$l > \frac{1}{17000}$  millim.  $= 6 \times 10^{-6}$  centim.; and the mean of four determinations of Quincke's for different substances give  $l > 6.1 \times 10^{-6}$  centimetres.

These results show that the radius of the intercommunicating capillaries necessary to give to the osmotic pressures of solutions the values which they possess by means of capillary action, lies well within the radius of capillary attraction; so that the whole section of liquid in the capillary would be urged by difference of surface-tension in the direction of the liquid of greater surface-tension, that is from the solvent towards the solution, and thus give rise to a difference of pressure, in other words cause osmotic pressure.

Consider, again, for a moment the relative values of the capillary openings here calculated, and that found as a minimum for the radius of capillary action. The former is  $18 \times 10^{-7}$  and the latter  $6 \times 10^{-6}$  centimetres; and it follows that, under the given conditions, the capillary opening is smaller than the radius of capillary action, and hence only a portion of the surface-tension will come into action, viz. that acting up to the radius of the capillary instead of to the radius of capillary action. So that the value of  $T$  in the equation  $r = \frac{2T}{P}$  will be diminished, and  $r$  will have a still smaller value than that

calculated for it above. This alteration in the value of  $T$  will not be so great as the ratios of the two values  $6 \times 10^{-6}$  and  $18 \times 10^{-7}$  indicate; for the value of the force of molecular attraction varies inversely as some high power of the distance, according to Laplace inversely as the fifth power of the distance. And it is the portions where the molecular attraction has its smaller values that are shut out as the capillary gradually narrows past the value of  $6 \times 10^{-6}$  centimetres.

It follows from these considerations that the capillaries or pores must have a radius of somewhat less than  $18 \times 10^{-7}$  centimetres. Now it has been determined by several different methods that the diameters of molecules lie between  $10^{-7}$  and  $10^{-8}$  centimetres; and it is extremely probable that this is the value to which the diameters of these capillary openings in semipermeable walls must approximate. This result is rendered probable, not only by the reasoning here given, but by the experimental method employed for producing such semipermeable walls, by producing an insoluble precipitate in the minute channels of a porous cell. It seems reasonable to suppose that after such a process communication takes place only in the intramolecular spaces or meshes of the precipitate, and such meshes must have about the dimensions found for them by the theoretical considerations here given.

If the molecules of the solvent do pass in this manner, in single file as it were, through the innumerable intramolecular spaces of the precipitate forming the semipermeable wall, it follows that the molecular attraction will have a constant maximum value, viz. its value just at the surface; and therefore, provided the meshes are so small that the molecules of the solvent can only pass through in single file, the osmotic pressure is unaffected by variations in the diameter of the intramolecular meshes. In fact in this condition, instead of a surface-tension acting only for a short distance inward from the perimeter and rapidly falling off in amount, there is a constant molecular attraction acting over the entire cross section and of maximum value; and instead of the equation  $2\pi rT = \pi r^2P$ , the equation  $\pi r^2\tau = \pi r^2P$  or  $\tau = P$ , where  $\tau$  is the difference in this maximum value for solution and solvent, holds, which shows that the osmotic pressure really is equal to the difference between the molecular attractions at the surface-layer of molecules of the solution and of the pure solvent.

With regard to the support furnished by experiment for connecting osmotic pressure with surface-tension, it may be premised that all experiments made on salt or other solutions in water or other solvents have been made with strong solutions, normal and multiples of normal; and it cannot be

expected that the laws deducible theoretically for the surface-tensions of such solutions can be proven more rigorously than they can in the case of such concentrated solutions for the allied phenomena of solution, such as lowering of vapour-pressure and depression of freezing-point.

It will be better to tabulate the results that may be expected to follow in case surface-tension is as closely connected, as here suggested, with osmotic pressure and the other solution phenomena, before discussing them.

(1) The surface-tensions of all solutions, obeying the other solution laws, should be higher than those of the solvents.

(2) For solutions of the same substance in the same solvent, the surface-tension, after correcting for dissociation, should increase directly as the concentration within certain limits of concentration, that is to say, within the same limits as those within which osmotic pressure obeys the gas law.

(3) For solutions of different substances in the same solvent, after correcting for dissociation, the differences in surface-tension between solution and solvent should be the same for equi-molecular solutions of these different substances.

(4) For equi-molecular solutions of either the same substance or different substances in different solvents, after correction for different amounts of dissociation in the different solvents, the differences in surface-tension in each case between the solvent and its solution must be equal, no matter how the surface-tensions of the different solvents may vary.

The only exception to the first law seems to be that of solutions of liquids, themselves possessing surface-tensions of their own, in water and in other liquids; in all such cases the surface-tension lies between the surface-tension of the components. But this is not a real exception: such solutions do not obey the vapour-pressure law either; the vapour-pressure of a solution of alcohol in water is not lower, but higher than that of pure water. On the other hand, all salt-solutions, both in water and other solvents, have a surface-tension higher than that of the solvent.

With regard to the second law, Quincke\* found, although working with concentrated solutions, that the increase in surface-tension is very nearly directly proportional to the concentration of the solution, and this result is confirmed by Volkmann†.

Upon the third law the experimental evidence varies. Quincke‡ and the earlier experimenters state the law that

\* Pogg. *Ann.* clx. pp. 337, 560.

† Wied. *Ann.* xvii. p. 353 (1882); xxviii. p. 135 (1886).

‡ *Vide l. c.*

the increase in surface-tension is the same for equi-equivalent not equi-normal solutions as the law here described requires; but their results were uncorrected for dissociation, and besides do not agree very closely with the law given by these observers, when so corrected (by dividing the increase in each case by the corresponding value of Arrhenius's coefficient of dissociation  $i$ ); they agree almost as closely with one law as the other, and cannot be said to agree with either.

In considering this point of variance, it ought to be remembered that the experiments quoted were carried out with concentrated solutions; for which analogy teaches us, from a consideration of the irregularities shown in depression of freezing-point and vapour-pressure under like conditions, no close agreement can be expected; and besides the quantity to be measured, viz. a small variation in surface-tension, is infinitely more difficult to obtain accurately than the corresponding quantities which are measured in freezing-point and boiling-point determinations, that is to say, than small differences in temperature.

In the case of dilute solutions these differences would become so small as to be impossible to measure with any approach to accuracy, so that from experimental difficulties this deduction cannot be tested with certainty.

Goldstein\*, in a recent paper, states a law which, though expressed differently, is practically the same as the third deduction here given, viz.:—In solutions of equal percentage concentration the difference in capillary rise is proportional, after correction for dissociation, to the molecular weight. But as there is no account whatever taken of the densities of the solutions, and the correction for dissociation is made by multiplying the observed difference in capillary rise by  $i$ , Arrhenius's Coefficient of Dissociation, instead of, as all reasoning and analogy show ought to be done, dividing by that factor, it does not seem to me that much reliance can be placed on the result.

The results given by Quincke for solutions of chlorides in water and alcohol are, when corrected for dissociation, in remarkably close agreement with the fourth deduction stated above.

Quincke's† figures give as the increase in surface-tension of a normal solution of lithium chloride in water, 1.534 dynes per centimetre, and for a normal solution of the same salt in

\* *Zeitschrift für physikalische Chemie*, v. p. 233 (1890).

† *Pogg. Ann.* clx. p. 560.



alcohol an increase of .968 dyne per centimetre. Correcting the former result for dissociation, the result is a rise corresponding to .953 dyne for a non-dissociated substance in water; and the number .968 for solution in alcohol would undergo but a slight diminution on account of the very small amount of dissociation in alcoholic solution.

Thus it appears that the rise, after this correction has been applied, is almost the same for these two solvents, as it ought to be in accordance with the fourth of the theoretical deductions stated above.

### XXXIII. On the Minimum Current audible in the Telephone. By Lord RAYLEIGH, Sec.R.S.\*

THE estimates which have been put forward of the minimum current perceptible in the Bell telephone vary largely. Mr. Preece gives  $6 \times 10^{-13}$  ampere†; Prof. Tait, for a current reversed 500 times per second,  $2 \times 10^{-12}$  ampere‡. De la Rue gives  $1 \times 10^{-8}$  ampere, and the same figure is recorded by Brough§ as applicable to the *strongest* current with which the instrument is worked. Various methods, more or less worthy of confidence, have been employed, but the only experimenter who has described his procedure with detail sufficient to allow of criticism is Prof. Ferraris||, whose results may be thus expressed:—

Pitch.	Frequency.	Minimum current in amperes.
Do <sub>3</sub> .....	264	$23 \times 10^{-9}$
Fa <sub>3</sub> .....	352	$17 \times 10^{-9}$
La <sub>3</sub> .....	440	$10 \times 10^{-9}$
Do <sub>4</sub> .....	528	$7 \times 10^{-9}$
Re <sub>4</sub> .....	594	$5 \times 10^{-9}$

The currents were from a make-and-break apparatus, and in each case are reckoned as if only the first periodic term of

\* Communicated by the Author, having been read at the Oxford Meeting of the British Association.

† Brit. Assoc. Report, Manchester, 1887, p. 611.

‡ Edin. Proc. vol. ix. p. 551 (1878). Prof. Tait speaks of a *billion* B.A. units, and, as he kindly informs me, a billion here means  $10^{12}$ .

§ Proceedings of the Asiatic Society of Bengal, 1877, p. 255.

|| *Atti della R. Accad. d. Sci. di Torino*, vol. xiii. p. 1024 (1877).

the Fourier series representative of the actual current were effective. On this account the quantities in the third column should probably be increased, for the presence of overtones could hardly fail to favour audibility.

Although a considerable margin must be allowed for varying pitch, varying acuteness of audition, and varying construction of the instruments, it is scarcely possible to suppose that all the results above mentioned can be correct, even in the roughest sense. The question is of considerable interest in connexion with the theory of the telephone. For it appears that *a priori* calculations of the possible efficiency of the instrument are difficult to reconcile with numbers such as those of Tait and of Preece, at least without attributing to the ear a degree of sensitiveness to aerial vibration far surpassing even the marvellous estimates that have hitherto been given\*.

Under these circumstances it appeared to be desirable to undertake fresh observations, in which regard should be paid to various sources of error that may have escaped attention in the earlier days of telephony. The importance of defining the resistance of the instruments and of employing pure tones of various pitch need not be insisted upon.

As regards resistance, a low-resistance telephone, although suitable in certain cases, must not be expected to show the same sensitiveness to current as an instrument of higher resistance. If we suppose that the total space available for the windings is given, and that the proportion of it occupied by the copper is also given, a simple relation obtains between the resistance and the minimum current. For if  $\gamma$  be the current,  $n$  be the number of convolutions, and  $r$  the resistance, we have, as in the theory of galvanometers,  $n\gamma = \text{const.}$ ,  $n^{-2}r = \text{const.}$ , so that  $\gamma\sqrt{r} = \text{const.}$ , or the minimum current is inversely as the square root of the resistance.

The telephones employed in the experiments about to be narrated were two, of which one ( $T_1$ ) is a very efficient instrument of 70-ohms resistance. The other ( $T_2$ ), of less finished workmanship, was rewound in the laboratory with comparatively thick wire. The interior diameter of the windings is 9 millim., and the exterior diameter is 26 millim. The width of the groove, or the axial dimension of the coil, is 8 millim., the number of windings is 160, and the resistance is .8 ohm. Since the dimensions of the coils are about the

\* Proc. Roy. Soc. vol. xxvi. p. 248 (1877). Also Wien, Wied. Ann. vol. xxxvi. p. 834 (1889).

same in the two cases, we should expect, according to the above law, that about 10 times as much current would be required in  $T_2$  as in  $T_1$ . Both instruments are of the Bell (unipolar) type, and comparison with other specimens shows that there is nothing exceptional in their sensibility.

In view of the immense discrepancies above recorded, it is evident that what is required is not so much accuracy of measurement as assured soundness in method. It appeared to me that electromotive forces of the necessary harmonic type would be best secured by the employment of a revolving magnet in the proximity of an inductor-coil of known construction. The electromotive force thus generated operates in a circuit of known resistance; and, if the self-induction can be neglected, the calculation of the current presents no difficulty. The sound as heard in the telephone may be reduced to the required point either by varying the distance (B) between the magnet and the inductor, or by increasing the resistance (R) of the circuit. In fact both these quantities may be varied; and the agreement of results obtained with widely different values of R constitutes an effective test of the legitimacy of neglecting self-induction. When R is too much reduced, the time-constant of the circuit becomes comparable with the period of vibration, and the current is no longer increased in proportion to the reduction of R. This complication is most likely to occur when the pitch is high.

In order to keep as clear as possible of the complication due to self-induction, I employed in the earlier experiments a resistance-coil of 100,000 ohms, constructed as usual of wire doubled upon itself. But it soon appeared that in avoiding Scylla I had fallen upon Charybdis. The first suspicion of something wrong arose from the observation that the sound was nearly as loud when the 100,000 ohms was included as when a 10,000-ohm coil was substituted for it. The first explanation that suggested itself was that the sound was being conveyed mechanically instead of electrically, as is indeed quite possible under certain conditions of experiment. But a careful observation of the effect of breaking the continuity of the leads, one at a time, proved that the propagation was really electrical. Subsequent inquiry showed that the anomaly was due to a condenser, or leyden, like action of the doubled wire of the 100,000-ohm coil. When the junction at the middle was unsoldered, so as to interrupt the metallic continuity, the sounds heard in the telephone were nearly as loud as before. In this condition the resistance should have been

enormous, and was in fact about 12 megohms \* as indicated by a galvanometer. It was evident that the coil was acting principally as a leyden rather than as a resistance, and that any calculation founded upon results obtained with it would be entirely fallacious.

It is easy to form an estimate of the point at which the complication due to capacity would begin to manifest itself. Consider the case of a simple resistance  $R$  in parallel with a leyden of capacity  $C$ , and let the currents in the two branches be  $x$  and  $y$  respectively. If  $V$  be the difference of potential at the common terminals, proportional to  $e^{ipt}$ , we have

$$x = V/R, \quad y = C \, dV/dt = ipVC;$$

so that

$$\frac{x+y}{V} = \frac{1+ipRC}{R}.$$

The amplitude of the total current is increased by the leyden in the ratio  $\sqrt{(1+p^2R^2C^2)} : 1$ ; and the action of the leyden becomes important when  $pRC=1$ . With a frequency of 640,  $p=4020$ ; so that, if  $R=10^{14}$  c.g.s., the critical value of  $C$  is  $\frac{1}{402} \times 10^{-15}$  c.g.s., or about  $\frac{1}{400}$  of a microfarad.

It will be seen that even if the capacity remained unaltered, a reduction of resistance in the ratio say of 10 to 1 would greatly diminish the complication due to condenser-like action; but perhaps the best evidence that the results obtained are not prejudiced in this manner is afforded by the experiments in which the principal resistance was a column of plumbago.

The revolving magnet was of clock-spring, about  $2\frac{1}{2}$  centim. long, and so bent as to be driven directly, windmill fashion, from an organ bellows. It was mounted transversely upon a portion of a sewing-needle, the terminals of which were carried in slight indentations at the ends of a U-shaped piece of brass. As fitted to the wind-trunk the axis of rotation was horizontal.

The inductor-coil, with its plane horizontal, was situated so that its centre was vertically below that of the magnet at distance  $B$ . Thus, if  $A$  be the mean radius of the coil,  $n$  the number of convolutions, the galvanometer-constant  $G$  of the coil at the place occupied by the magnet is given by

$$G = \frac{2\pi n A^2}{C^3}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

\* Doubtless the insulation between the wires should have been much higher.

where  $C^2 = A^2 + B^2$ ; and if  $m$  be the magnetic moment of the magnet, and  $\phi$  the angle of rotation, the mutual potential  $M$  may be represented by \*

$$M = G m \sin \phi. \quad (2)$$

If the frequency of revolution be  $p/2\pi$ ,  $\phi = pt$ ; and then

$$dM/dt = G m p \cos pt. \quad (3)$$

The expression (3) represents the electromotive force operative in the circuit. If the inductance can be neglected, the corresponding current is obtained on division of (3) by  $R$ , the total resistance of the circuit.

The moment  $m$  is deduced by observation of the deflexion of a magnetometer-needle from the position which it assumes under the operation of the earth's horizontal force  $H$ . If the magnet be situated to the east at distance  $r$ , and be itself directed east and west, the angular deflexion  $\theta$  from equilibrium is given by

$$\tan \theta = \frac{2m/r^3}{H}.$$

The relation between the angle  $\theta$  and the double deflexion  $d$  in scale-divisions, obtained on *reversal* of  $m$ , is approximately  $\theta = d/4D$ , where  $D$  is the distance between mirror and scale; so that we may take

$$m = \frac{H r^3 d}{8D}. \quad (4)$$

The amplitude of the oscillatory current, generated under these conditions, is accordingly

$$\frac{n\pi p H A^2 r^3 d}{4C^3 R D}. \quad (5)$$

If c.g.s. units are employed,  $H = \cdot 18$ .  $A$  must of course be measured in centimetres; but any units that are convenient may be used for  $r$  and  $C$ , and for  $d$  and  $D$ . The current will then be given in terms of the c.g.s. unit, which is equal to 10 amperes.

The inductor-coil used in most of the experiments is wound upon an ebonite ring, and is the one that was employed as the "suspended coil" in the determination of the electro-chemical equivalent of silver †. The number of convolutions ( $n$ ) is 242.

\* Maxwell, 'Electricity and Magnetism,' vol. ii. § 700.

† Phil. Trans. part ii. 1884, p. 421.

The axial dimension of the section is 1·4 centim., and the radial dimension is ·97 centim. The mean radius  $A$  is 10·25 centim., and the resistance is about  $10\frac{1}{2}$  ohms.

In making the observations the current from the inductor-coil was led to a distant part of the house by leads of doubled wire, and was there connected to the telephone and resistances. Among the latter was a plumbago resistance on Prof. F. J. Smith's plan \* of about 84,000 ohms; but in most of the experiments a resistance-box going up to 10,000 ohms was employed, with the advantage of allowing the adjustment of sound to be made by the observer at the telephone. The attempt to hit off the least possible sound was found to be very fatiguing and unsatisfactory; and in all the results here recorded the sounds were adjusted so as to be *easily* audible after attention for a few seconds. Experiment showed that the resistances could then be *doubled* without losing the sound, although perhaps it would not be caught at once by an unprepared ear. But it must not be supposed that the observation admits of precision, at least without greater precautions than could well be taken. Much depends upon the state of the ear as regards fatigue, and upon freedom from external disturbance.

The pitch was determined before and after an observation by removing the added resistance and comparing the loud sound then heard with a harmonium. The *octave* thus estimated might be a little uncertain. It was verified by listening to the beats of the sound from the telephone and from a nearly unisonant tuning-fork, both sounds being nearly pure tones.

When the magnet was driven at full speed the frequency was found to be 307, and at this pitch a series of observations was made with various values of  $C$  and of  $R$ . Thus when  $B=7\cdot75$  inches, or  $C=8\cdot7$  inches, the resistance from the box required to produce the standard sound in telephone  $T_1$  was 8000 ohms, so that  $R=8100 \times 10^9$ . The quantities required for the calculation of (5) are as follows:—

$$\begin{array}{lll} n=242, & p=2\pi \times 307, & H=.18, \\ A=10\cdot25, & r=8\cdot25, & d=140, \\ C=8\cdot7, & R=81 \times 10^{11}, & D=1370, \end{array}$$

$r$  and  $C$  being reckoned in inches,  $d$  and  $D$  in scale-divisions of about  $\frac{1}{40}$  inch. From these data the current required to

\* Phil. Mag. vol. xxxv. p. 210 (1893).

produce the standard sound is found to be  $7.4 \times 10^{-8}$  c.g.s., or  $7.4 \times 10^{-7}$  amperes, for telephone  $T_1$ .

The results obtained by the method of the revolving magnet are collected into the accompanying table. The "wooden coil" is of smaller dimensions than the "ebonite coil," the mean radius being only 3.5 centim. The number of convolutions is 370.

Frequency = 307. Ebonite coil.

Telephone.	R in ohms.	Current in amperes.	Sound.
$T_1$ ....	84100 Plumbago.	$3.8 \times 10^{-7}$	Below standard.
$T_1$ ....	8100 Box.	$7.4 \times 10^{-7}$	Standard.
$T_1$ ....	4100 Box.	$5.2 \times 10^{-7}$	.....
$T_2$ ....	500 Box.	$1.2 \times 10^{-5}$	.....
$T_2$ ....	200 Box.	$1.0 \times 10^{-5}$	.....

Frequency = 307. Wooden coil.

$T_1$ ....	84100 Plumbago.	$3.6 \times 10^{-7}$	Standard.
$T_1$ ....	10100 Box.	$3.7 \times 10^{-7}$	.....
$T_1$ ....	1600 Box.	$5.4 \times 10^{-7}$	.....
$T_2$ ....	350 Box.	$1.1 \times 10^{-5}$	.....

Frequency = 192. Ebonite coil.

$T_1$ ....	3100 Box.	$2.5 \times 10^{-6}$	Standard.
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The method of the revolving magnet seemed to be quite satisfactory so far as it went, but it was desirable to extend the determinations to frequencies higher than could well be reached in this manner. For this purpose recourse was had to magnetized tuning-forks, vibrating with known amplitudes. If, for the moment, we suppose the magnetic poles to be concentrated at the extremities of the prongs, a vibrating-fork may be regarded as a simple magnet, fixed in position and direction, but of moment proportional to the instantaneous distance between the poles. Thus, if the magnetic axis pass perpendicularly through the centre of the mean plane of the inductor-coil, the situation is very similar to that obtaining in the case of the revolving magnet. The angle  $\phi$  in (2) is no longer variable, but such that  $\sin \phi = 1$  throughout. On the other hand  $m$  varies harmonically. If  $l$  be the mean distance between the poles,  $2\beta$  the extreme arc from rest to rest traversed by each pole during the vibration,  $m_0$  the mean magnetic moment,

$$m/m_0 = 1 + 2\beta/l \cdot \sin pt,$$

and

$$dM/dt = Gm_0 p \cdot 2\beta/l \cdot \cos pt. \quad . \quad . \quad . \quad (6)$$

The formula corresponding to (5) is thus derived from it by simple introduction of the factor  $2\beta/l$ .

The forks were excited by bowing, and the observation of amplitude was effected by comparison with a finely divided scale under a magnifying-glass. It was convenient to observe the extreme end of a prong where the motion is greatest, but the double amplitude thus measured must be distinguished from  $2\beta$ . In order to allow for the distance between the resultant poles and the extremities of the prongs, the measured amplitude was reduced in the ratio of 2 to 3. The observation of the magnetic moment at the magnetometer is not embarrassed by the diffusion of the free polarity.

In order to explain the determination more completely, I will give full details of an observation with a fork  $c'$  of frequency 256. The distance  $l$  between the middles of the prongs was  $\cdot 875$  inch, and the double amplitude of the vibration at the end of one of the prongs was  $\cdot 09$  inch. Thus  $2\beta$  is reckoned as  $\cdot 06$  inch. The inductor-coil was the ebonite coil already described, and the sound was judged to be of the standard distinctness when, for example,  $B=15$  inches, or  $C=15\cdot 5$  inches, and the added resistance was 1000 ohms, so that  $R=1100 \times 10^9$ . The quantities required for the computation of (5) as extended are

$$\begin{aligned} n &= 242, & p &= 2\pi \times 256, & H &= \cdot 18, \\ A &= 10\cdot 25, & r &= 15, & d &= 410, \\ C &= 15\cdot 5, & R &= 11 \times 10^{11}, & D &= 1370, \\ & & 2\beta &= \cdot 06, & l &= \cdot 875; \end{aligned}$$

and they give for the current corresponding to the standard sound  $9\cdot 8 \times 10^{-8}$  c.g.s., or  $9\cdot 8 \times 10^{-7}$  amperes.

A summary of the results obtained with forks of pitch  $c, c', e', g', c'', e'', g''$  is annexed. As the pitch rose, the difficulties of observation increased, both on account of the less duration of the sound and of the smaller amplitudes available for measurement. In one observation with telephone  $T_2$  at pitch  $c''$ , the resistance, estimated at 11 ohms, was that of the coil, telephone, and leads only. No trustworthy result was to be expected under such conditions, but the number is included in order to show how small was the influence of self-induction, even where it had every opportunity



Telephone.                      R in ohms.                      Current in amperes.

$$c = 128.$$

$T_1$ ....	1100 ....	$2.8 \times 10^{-5}$
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$$c' = 256.$$

$T_1$ ....	8100 Box.	$6.8 \times 10^{-7}$	
$T_1$ ....	1100 ....	$9.8 \times 10^{-7}$	
$T_2$ ....	500 ....	.....	$1.1 \times 10^{-5}$

$$e' = 320.$$

$T_1$ ....	84000 Plumb.	$3.8 \times 10^{-7}$
$T_1$ ....	6100 Box.	$2.6 \times 10^{-7}$
$T_1$ ....	1600 ....	$3.1 \times 10^{-7}$

$$g' = 384.$$

$T_1$ ....	84000 Plumb.	$1.4 \times 10^{-7}$	
$T_1$ ....	9500 Box.	$1.6 \times 10^{-7}$	
$T_1$ ....	2100 ....	$1.4 \times 10^{-7}$	
$T_1$ ....	900 ....	$1.7 \times 10^{-7}$	
$T_2$ ....	600 ....	.....	$1.9 \times 10^{-6}$
$T_2$ ....	300 ....	.....	$2.2 \times 10^{-6}$

$$c'' = 512.$$

$T_1$ ....	84000 Plumb.	$8.9 \times 10^{-8}$	
$T_1$ ....	9000 Box.	$4.8 \times 10^{-8}$	
$T_1$ ....	3600 ....	$5.2 \times 10^{-8}$	
$T_1$ ....	700 ....	$8.2 \times 10^{-8}$	
$T_2$ ....	11?	.....	$5.2 \times 10^{-6}?$
$T_2$ ....	100 Box.	.....	$1.9 \times 10^{-6}$
$T_2$ ....	300 ....	.....	$1.4 \times 10^{-6}$
$T_2$ ....	500 ....	.....	$2.5 \times 10^{-6}$
$T_2$ ....	900 ....	.....	$2.4 \times 10^{-6}$

$$e'' = 640.$$

$T_1$ ....	84000 Plumb.	$3.8 \times 10^{-8}$
$T_1$ ....	5100 Box.	$3.8 \times 10^{-8}$
$T_1$ ....	1100 ....	$5.5 \times 10^{-8}$

$$g'' = 768.$$

$T_1$ ....	84000 Plumb.	$1.1 \times 10^{-7}$
$T_1$ ....	7100 Box.	$.9 \times 10^{-7}$
$T_1$ ....	2100 ....	$1.1 \times 10^{-7}$

of manifesting itself. If we bring together the numbers\* derived with the revolving magnet and with the forks, we obtain in the case of  $T_1$ :—

Pitch.	Source.	Current in $10^{-8}$ amperes.
128 ....	Fork.....	2800
192 ....	Revolving magnet ..	250
256 ....	Fork.....	83
307 ....	Revolving magnet ..	49
320 ....	Fork.....	32
384 ....	.....	15
512 ....	.....	7
640 ....	.....	4.4
768 ....	.....	10

It would appear that the maximum sensitiveness to current occurs in the region of frequency 640; but observations at still higher frequencies would be needed to establish this conclusion beyond doubt. Attention must be paid to the fact that the sounds were not the least that could be heard, and that before a comparison is made with the numbers given by other experimenters there should be a division by 2, if not by 3. But this consideration does not fully explain the difference between the above table and that of Ferraris already quoted, from which it appears that in his experiments a current of  $5 \times 10^{-9}$  amperes was audible.

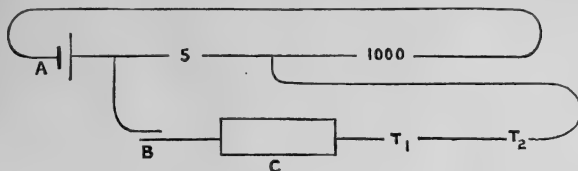
It is interesting to note that the sensitiveness of the telephone to periodic currents is of the same order as that of the galvanometer of equal resistance to steady currents†, viz. that the currents (at pitch 512) just audible in the telephone would, on commutation, be just easily visible by a deflexion in the latter instrument. But there is probably more room for further refinements in the galvanometer than in the telephone.

If we compare the performances of the two telephones  $T_1$  and  $T_2$ , we find ratios of sensitiveness to current ranging from 13 to 30; so that  $T_2$  shows itself inferior in a degree beyond what may be accounted for by the resistances. It is singular that an experiment of another kind led to the opposite conclusion. The circuit of a Daniell cell A was permanently closed through resistance-coils of 5 ohms and of 1000 ohms. The two telephones in series with one another and with a resistance-box C were placed in a derived circuit where was

\* The observations recorded were made with my own ears. Mr. Gordon obtained very similar numbers when he took my place.

† See, for example, Ayrton, Mather, and Sumpner, *Phil. Mag.* vol. xxx. p. 90, 1890, "On Galvanometers."

also a scraping contact-apparatus B, as indicated in the figure. The adjustment was made by varying the resistance in C until the sound was just easily audible in the telephone under trial. Experiments conducted upon this plan showed that  $T_1$  was only about five times as sensitive to current as  $T_2$ . It was



noticed, however, that the sounds, though as equal as could be estimated, were not of the same quality, and in this probably lies the explanation of the discrepancy between the two methods of experimenting. In the latter the original sound is composite, and the telephone selects the most favourable elements—that is, those nearly in agreement with the natural pitch of its own plate. In this way the loudness of the selected sound becomes a question of the freedom of vibration of the plate, an element which is almost without influence when the sound is of pitch far removed from that of the proper tone of the telephone. There was independent reason for the suspicion that  $T_1$  had not so well defined a proper pitch as was met with in the case of some other telephones.

*P.S.*—Measurements with the electro-dynamometer have been made by Cross and Page\* of the currents used in practical telephony. The experiments were varied by the employment of several transmitters, and various vowel sounds were investigated. The currents found were of the order  $2 \times 10^{-4}$  amperes.

XXXIV. *An Attempt at a Quantitative Theory of the Telephone.* By Lord RAYLEIGH, Sec. R.S.†

THE theory of the telephone cannot be said to be understood, in any but the most general manner, until it is possible to estimate from the data of construction what its sensitiveness should be, at least so far as to connect the magnitude of the vibratory current with the resulting condensations and rarefactions in the external ear-passage.

\* Electrical Review, Nov. 14, 1885. I owe this reference to Mr. Swinburne.

† Communicated by the Author, having been read at the Oxford Meeting of the British Association.

Unfortunately such an estimate is a matter of extreme difficulty, partly on account of imperfection in our knowledge of the magnetic properties of iron, and partly from mathematical difficulties arising from the particular forms employed in actual construction; and indeed the problem does not appear to have been attacked hitherto. In view, however, of the doubts that have been expressed as to theory, and of the highly discrepant estimates of actual sensitiveness which have been put forward, it appears desirable to make the attempt. It will be understood that at present the question is as to the order of magnitude only, and that the result will not be without value should it prove to be 10 or even 100 times in error.

One of the elements required to be known, the number ( $n$ ) of convolutions, cannot be directly observed in the case of a finished instrument; but it may be inferred with sufficient accuracy for the present purpose from the dimensions and the *resistance* of the coil. Denote the axial dimension by  $\xi$ , the inner and outer radii by  $\eta_1$  and  $\eta_2$ , the section of the wire by  $\sigma$  and its total length by  $l$ , so that  $l\sigma$  is the total volume of copper. The area of section of the coil by an axial plane is  $\xi(\eta_2 - \eta_1)$ , and of this the area  $n\sigma$  is occupied by copper. If we suppose the latter to be *half* the former, we shall not be far from the mark. Thus

$$n\sigma = \frac{1}{2}\xi(\eta_2 - \eta_1). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

On the same assumption,

$$l\sigma = \frac{1}{2}\pi\xi(\eta_2^2 - \eta_1^2). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Accordingly, if  $R$  be the whole resistance of the coil, and  $r$  the specific resistance of copper,

$$R = r \frac{l}{\sigma} = \frac{2\pi r n^2 (\eta_2 + \eta_1)}{\xi(\eta_2 - \eta_1)}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As applicable to actual telephones we may take  $\xi = 1$  centim.,  $\eta_2 = 3\eta_1$ ; and then  $R = 4\pi r n^2$ . In c.g.s. measure  $r = 1600$ , and thus

$$n^2 = \frac{R}{4\pi \times 1600}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If the resistance be 100 ohms,

$$R = 10^{11}, \text{ and } n = 2230.$$

When the resistance varies, other circumstances remaining the same,

$$n \propto \sqrt{R}.$$

We have now to connect the periodic force upon the tele-

phone-plate with the periodic current in the coil. As has already been stated, only a very rough estimate is possible *a priori*. We will commence by considering the case of an unlimited cylindrical core, divided by a transverse fracture into two parts, and encompassed by an infinite cylindrical magnetizing coil containing  $n$  turns to the centimetre. If  $\gamma$  be the current, the magnetizing force  $\delta H$  due to it is

$$\delta H = 4\pi n\gamma. \quad (5)$$

If we regard the core as composed of soft iron, magnetized strongly by a constant force  $H$ , the mechanical force with which the two parts attract one another per unit of area is in the usual notation

$$I(H + 2\pi I);$$

and what we require is the variation of this quantity, when  $H$  becomes  $H + \delta H$ . This may be written

$$\delta H \left\{ I + (H + 4\pi I) \frac{dI}{dH} \right\}. \quad (6)$$

The value of  $dI/dH$  to be here employed is that appropriate to small cyclical changes. It is greatest when  $I$  is small, and then\* amounts to about  $100/4\pi$ . As  $I$  increases,  $dI/dH$  diminishes, and finally approaches to zero in the state of saturation. In order to increase (6) it is thus advisable to augment  $I$  up to a certain point, but not to approach saturation so nearly as to bring about a great diminution in the value of  $dI/dH$ . In the absence of precise information we may estimate that the maximum of (6) will be reached when  $I$  is about half the saturation value, or equal to  $800\ddagger$ ; and that  $dI/dH$  also has half its maximum value, or  $50/4\pi$ . At this rate the force due to  $\delta H$  is about  $40,000\delta H$ , reckoned per unit of area of the divided core, or by (5)

$$40,000 \times 4\pi n\gamma. \quad (7)$$

But before (7) can be applied to the core of a telephone electromagnet it must be subjected to large deductions. For in the telephone the total number of windings  $n$  is limited to about one centimetre measured parallel to the axis, whereas in (7) the electromagnet is supposed to be infinitely long, and  $n$  denotes the number of windings *per* centimetre. If we are to suppose in (7) that the windings are really limited to one centimetre, lying immediately on one side of the division, there must be a loss of effect which I estimate at 5 times.

\* Phil. Mag. xxiii. p. 225 (1887).

† Ewing, 'Magnetic Induction,' 1891, p. 136.

We have now further to imagine the second part of the divided cylinder to be replaced by the plate of the telephone, and that not in actual contact with the remaining cylindrical part. The reduction of effect on this account I estimate at 4 times\*. The force on the telephone-plate per unit area of core is thus

$$2000 \times 4\pi n\gamma; \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or if, as for the telephone of 100-ohms resistance,  $n=2200$ , and area of section =  $\cdot 31$  sq. cm.,

$$\text{force} = 1.7 \times 10^7 \gamma. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In (9) the force is in dynes, and the current  $\gamma$  is in c.g.s. measure. If  $\Gamma$  denote the current reckoned in amperes,

$$\text{force} = 1.7 \times 10^6 \Gamma, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and this must be supposed to be operative at the centre of the plate.

We shall presently consider what effect such a force may be expected to produce; but before proceeding to this I may record the result of some experiments directed to check the applicability of (10), and made subsequently to the theoretical estimates. A Bell telephone, similar to  $T_1$ , was mounted vertically, mouth downwards, having attached to the centre of its plate a slender strip of glass. This strip was also vertical and carried at its lower end a small scale-pan. The whole weight of the attachments was only  $\cdot 44$  gram. The movement of the glass strip in the direction of its length was observed through a reading-microscope focused upon accidental markings. The telephone, itself of 70-ohms resistance, was connected through a reversing-key with a Daniell cell and with an external resistance varied from time to time. In taking an observation the current was first sent in such a direction as to depress the plate, and the web was adjusted upon the mark. The current was then reversed, by which the plate was drawn up, but by addition of weights in the pan it was brought back again to the *same* position as before. The force due to the current is thus measured by the *half* of the weight applied.

The results were as follows:—

External resistance in ohms . .	100	200	500
Weight in grams . . . . .	8	4	2

When 1000 ohms were included, the displacement on reversal

\* I should say that these estimates were all made in ignorance of the result to which they would lead.

was still just visible. We may conclude that a force of 1 gram weight corresponds to a current of about  $\frac{1}{600}$  of an ampere. Now, 1 gram weight is equal to 981 dynes, so that for comparison with (10)

$$\text{force} = .6 \times 10^6 \Gamma. \quad . \quad . \quad . \quad . \quad (11)$$

The force observed is thus about the third part of that which had been estimated, and the agreement is sufficient.

Although not needed for the above comparison, we shall presently require to know the linear displacement of the centre of the telephone-plate due to a given force. Observations with the aid of a micrometer-eyepiece showed that a force of 5 grams weight gave a displacement of  $10^{-4} \times 6.62$  centim., or  $10^{-4} \times 1.32$  for each gram, viz.  $10^{-7} \times 1.34$  centim. per dyne. Thus by (11) the displacement  $x$  due to a current  $\Gamma$  expressed in amperes is

$$x = .080 \Gamma. \quad . \quad . \quad . \quad . \quad (12)$$

We have now to estimate what motion of the telephone-plate may be expected to result from a given periodic force operating at its centre. The effect depends largely upon the relation between the frequency of the imposed vibration and those natural to the plate regarded as a freely vibrating body. If we attempt to calculate the natural frequencies *a priori*, we are met by uncertainty as to the precise mechanical conditions. From the manner in which a telephone-plate is supported we should naturally regard the ideal condition as one in which the whole of the circular boundary is *clamped*. On this basis a calculation may be made, and it appears\* that the frequency of the gravest symmetrical mode should be about 991 in the case of the telephone in question. But it may well be doubted whether we are justified in assuming that the clamping is complete, and any relaxation tells in the direction of a lowered frequency. A more trustworthy conclusion may perhaps be founded upon the observed connexion between displacement and force of restitution, coupled with an estimate of the inertia of the moving parts. The total weight of the plate is 3.4 grams; the outside diameter is 5.7 centim., and the inside diameter, corresponding to the free portion of the plate, is 4.5. The effective mass, supposed to be situated at the centre, I estimate to be that corresponding to a diameter of 2.5 centim., viz. .65 gram. A force of restitution per unit displacement equal to  $(10^{-7} \times 1.34)^{-1}$ , or  $10^6 \times 7.5$ , is supposed to urge the above mass to its position

\* 'Theory of Sound,' 2nd ed. § 221 *a*.

of equilibrium. The frequency of the resulting vibration is

$$\frac{1}{2\pi} \sqrt{\left\{ \frac{10^6 \times 7.5}{.65} \right\}} = 541.$$

With the aid of a special electric maintenance the plate may be made to *speak* on its own account. The frequency so found, viz. 896, corresponds undoubtedly to a free vibration, but it does not follow that the vibration is the gravest of which the plate is capable; and there were indications pointing to the opposite conclusion.

As it is almost impossible to form an *a priori* estimate of the amplitude of vibration ( $x$ ) when the frequency of the force is in the neighbourhood of any of the free frequencies, I will take for calculation the case of frequency 256, which is presumably much lower than any of them. Under these circumstances an "equilibrium theory" may be employed, the displacement coexisting with any applied force being the same as if the force were permanent. At this pitch the minimum current recorded in the table\* is  $8.3 \times 10^{-7}$  amperes; so that by (12) the maximum excursion corresponding thereto is given by  $x = .080 \times 8.3 \times 10^{-7} = 6.8 \times 10^{-8}$  centim.

The excursion thus found must not be compared with that calculated formerly† for free progressive waves. The proper comparison is rather between the *condensations*  $s$  in the two cases. In a progressive wave the connexion between  $s$  and  $v$ , the maximum velocity, is  $v = as$ , where  $a$  is the velocity of propagation. But in the present case the excursion  $x$  takes effect upon a very small volume. If  $A$  be the effective area of the plate, and  $S$  the whole volume included between the plate and the tympanum of the ear, we may take  $s = Ax/S$ . This relation assumes that the condensations and rarefactions are uniform throughout the space in question, an assumption justified by the smallness of its dimensions in comparison with the wave-length, and further that the behaviour is the same as if the space were closed air-tight. It would seem that a slight deficiency in the latter respect would not be material.

For the numerical application I estimate that  $A = 4$  sq. centim.,  $S = 20$  cub. centim.; so that with the above value of  $x$

$$s = 1.4 \times 10^{-8}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$s$  being reckoned in atmospheres.

\* *Supra*, p. 294.

† *Proc. Roy. Soc.* vol. xxxvi. p. 248 (1877).



The value of  $s$  corresponding to but just audible progressive waves of frequency 256 was found to be  $5.9 \times 10^{-9}$ , in sufficiently good agreement with (13) \*.

But if the equilibrium theory be applied to the notes of higher pitch, such as 512, we find the actual sensitiveness of the telephone greater than according to the calculation. In this case  $\dagger \Gamma = 7 \times 10^{-8}$ ; so that by (12)

$$x = 5.6 \times 10^{-9},$$

and

$$s = Ax/S = 1.1 \times 10^{-9}, \dots \dots (14)$$

decidedly smaller than that ( $4.5 \times 10^{-9}$ ) deduced from the observations upon progressive waves. The conclusion seems to be that for these frequencies the equilibrium theory of the telephone-plate fails, and that in virtue of resonance the sensitiveness of the instrument is specially exalted.

I will not dwell further upon these calculations, which involve too much guesswork to be very satisfactory. They suffice, however, to show that the "push and pull" theory is capable of giving an adequate account of the action of the telephone, so far at least as my own observations are concerned. But it is doubtful, to say the least, whether it could be reconciled with estimates of sensitiveness such as those of Tait and of Preece.

XXXV. *Experiments on the Relations of Pressure, Volume, and Temperature of Rarefied Gases.* By E. C. C. BALY, 1851 Exhibition-Scholar in University College, London, and WILLIAM RAMSAY, Ph.D., F.R.S.†

[Plate XI.]

THE experiments of which we give an account in the following pages are of two kinds:—first, they relate to the trustworthiness of measurements by means of the McLeod gauge; and second, they deal with the thermal expansion of gases at low pressures. The behaviour of the ingenious gauge invented by Professor Herbert McLeod has, so far as we know, not been carefully investigated. The thermal expansion of gases at low pressures has been the subject of two investigations, one by Mendeléeff, and one by G. Melander. But many researches have been made on the relations of volume

\* I hope shortly to publish an account of the observations upon which this statement is founded.

† *Supra*, p. 294.

‡ Communicated by the Physical Society: read June 8, 1894.

to pressure at constant temperatures; and as there is an intimate connexion between the compressibility of gases and their thermal expansion, we think it desirable to give a short summary of the work which has already been done on the subject. It is obvious that if the product of pressure and volume of a gas diminishes with the degree of rarefaction, it is to be expected that its coefficient of expansion with rise of temperature will increase; whereas, if the  $p v$  increases as observed by Mendeléeff and others, its coefficient of expansion will probably diminish.

### HISTORICAL RÉSUMÉ.

#### 1. Relation of Volume to Pressure at Constant Temperature.

For more than twenty years the question of the validity of Boyle's Law, applied to rarefied gases, has been the subject of frequent articles in scientific journals. In 1873 Siljeström (*Bihang till K. Svenska Vet. Akad. Handlingar*, ii. p. 1) published in Swedish an account of experiments to test this important law. His method consisted in exhausting one of two stout cylindrical metal vessels connected together by means of a tube provided with an air-tight stopcock. Both vessels were placed in a large reservoir of melting ice in order to maintain temperature constant at  $0^{\circ}$ . Each vessel was provided with a mercury manometer; and while the larger of the two had no opening except the tube already mentioned, which connected it with the smaller vessel, the latter was joined by means of a brass tube with a stopcock to an ordinary exhausting air-pump, also furnished with a mercury gauge.

The plan of operation was as follows:—The pressure of gas in the smaller vessel was reduced by means of the air-pump, communication with the larger vessel being cut off by means of the stopcock, and the pressure of the gas in both vessels was read on the mercury gauges attached to them, and also on that attached to the air-pump. The pressure registered by the gauge of the smaller vessel and by the air-pump gauge should of course be the same. Communication with the air-pump was then shut off. The stopcock between the two vessels was then opened, and gas passed from the larger to the smaller. After time had been allowed for equilibrium of temperature and pressure to be re-established, the pressures on the gauges were again read. The capacities of the vessels being accurately known, the product of pressure and volume could be calculated.

Sixteen series of experiments, each consisting of fourteen

individual readings, were made with air; the diminution of pressure varied in these series from that of the atmosphere to 1.4 millim.; and by means of an accurate cathetometer the pressure was read to the second decimal place. The ratio of  $V$  (the volume of the closed reservoir) to  $V + V'$  (that of both reservoirs) was calculated by means of the formula

$$E' = \frac{E(V + n\mu)}{V + V' + n'\mu} = \frac{eV'}{V + V' + n'\mu},$$

where

$E$  is the original pressure of the gas;

$e$ , pressure read on gauge of second cylinder or of air-pump after exhausting;

$E'$ , pressure in cylinders after opening the stopcock;

$n\mu$  and  $n'\mu$ , small corrections introduced, due to alteration in total volume of apparatus owing to rise of mercury in the gauges.  $n$  is a number of centimetres,  $\mu$  the capacity of one centim. of the gauge.

$\beta$  (in following equation) =  $\mu/V$ . Hence

$$\frac{V'}{V} = \frac{E(1 + n\beta) - E'(1 + n'\beta)}{E' - e}.$$

If the ratio  $(V + V')/V$  remains constant, Boyle's law holds; if, on the contrary,  $(V + V')/V$  be too great or too small, the pressure  $E'$  would be either less or greater than corresponds with Boyle's law.

The results were averaged, series  $a$  and  $b$  being compared with series  $c$  and  $d$ ; the latter with series  $e$  and  $f$ , and so on. This process yielded six sets of average values of  $(V + V')/V$  for air. The results follow:—

Extremes of pressure.				$V + V'/V$ .
759	and	352	millim.	. . 1.47209
352	„	164	„	. . 1.47165
164	„	77	„	. . 1.46887
77	„	37	„	. . 1.46870
37	„	18	„	. . 1.46122
18	„	7	„	. . 1.46511

These values of  $V + V'/V$  decrease with falling pressure; the higher its value the lower the value of  $E'$ , and *vice versa*. Assuming from Regnault's observations between 1 and 30 atmospheres that at a pressure of 1 atmosphere the value given above, 1.47209, is correct, and that Boyle's law holds under such a pressure, it follows that the  $p v$  of the air increases with decreased pressure. This conclusion, too, Siljeström

considers to be rendered probable by Regnault's own work. For he, too, found that air is up to a certain degree more compressible at pressures higher than that of the atmosphere. For example, if Regnault's results for pressures between 3 and 6, between 6 and 12, and between 12 and 24 atmospheres be termed  $k'$ ,  $k''$ , and  $k'''$  respectively, then

$$k''/k' = 0.997128; \quad k'''/k'' = 0.999386.$$

The question of course is, Can these and similar ratios increase to above unity?

Siljeström found from similar but less numerous experiments with oxygen and with carbon dioxide that the variation in the ratio  $(V + V')/V$  was in the same direction. His results with hydrogen are:—1.47247 at 759–351 millim.; 1.47302 at 351–162 millim.; 1.47258 at 162–75 millim.; and 1.46895 at 75–17 millim.

Siljeström's results are criticised by Mendeléeff and by Amagat. Any error which he might have made is cumulative, as pointed out by Van der Ven, whose work will be subsequently considered.

Mendeléeff's work is at present unfinished, or at least a description of it in full has not yet appeared. His main work appeared in Russian in 1875, and the first part consists of 267 pages folio; the second part is not yet published. We owe to the kindness of Dr. Jas. Walker an account of the contents of this large volume. Short accounts of Mendeléeff's general conclusions are to be found in French in the *Mélanges Physiques et Chimiques tirés du Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg*, ix.; also *Annales de Chimie et Physique*, [3] ix. 1876. These abstracts leave much to be desired.

Mendeléeff states that he tried nearly a dozen different forms of apparatus before a satisfactory one was devised. This, he says, is figured in volume ii. table 15 (unpublished)\*; but he gives the following description of it in a lecture delivered before the Imperial Russian Technical Society in January 1881. It consisted of an ovoid glass vessel, with a capacity of about  $3\frac{1}{2}$  litres, placed in a trough of water. The lower portion of this vessel terminated in a tube, one metre in length, provided at its lower end with a stopcock; the volume of air was determined by weighing the mercury run out from this vessel. A tube was sealed to this vertical tube, which served to fill the measuring-vessel with mercury when required. A capillary tube was attached to the upper part of the

\* Professor Mendeléeff informs us that a large part of the second volume is now in manuscript.

measuring-vessel ; it communicated with two lateral descending tubes, through one of which gas could be introduced at will. It was closed by raising a reservoir of mercury, and covering an opening more than thirty inches below the top of the measuring-vessel ; but when the reservoir was lowered, gas could be passed into the measuring-vessel, through the capillary tube. The second descending tube connected the measuring-vessel with a wide manometer formed like a siphon ; and by means of a reservoir it was possible to raise the mercury in the open limb to a mark with great accuracy. Corrections were introduced for temperature, measured by a differential air-thermometer, and also for the varying volume of the apparatus due to the different heights of the mercury in the manometer. It is easy to see how this apparatus could be employed to test Boyle's law. To test Gay-Lussac's, he describes the operation thus :—

“The mercury is run out of the measuring-vessel to a mark on the capillary tube, and weighed. Let this be done at the temperature of boiling water. Now cool the bath to  $0^{\circ}$  by surrounding the vessel with ice—the pressure begins to diminish as is indicated by the manometer ; but we will not allow it to do so. By means of the stopcock and the other capillary, we let mercury run into the vessel until the pressure of the gas at  $0^{\circ}$  becomes the same as it was at  $100^{\circ}$ . The apparatus is then raised to the ordinary temperature, and the mercury which entered the tube at  $0^{\circ}$  is run out and weighed. This weight and the previous one give us the data necessary for calculating the true coefficient of expansion of gases.”

No final numbers are given in Mendeléeff's published papers, so far as we have been able to discover ; but the general result is stated thus :—

The product of pressure into volume,  $pv$ , which according to Boyle's law should be constant, varies considerably with diminution of pressure ; at low pressures  $pv/dp$  is positive, *i. e.* the gas is less compressible than it would be if it followed Boyle's law. Stating the case broadly, it may be said that at low pressures gases approach the state of a liquid or a solid ; or  $pv$  increases with decrease of  $p$  ; or  $e/d$  increases, for  $d=1/v$ .

We have thought it advisable to give a tolerably full description of Siljeström's and Mendeléeff's experiments, because they are described in languages not generally known ; we may discuss the remaining researches on the subject in much shorter space, seeing that they are described in French and in German.

Amagat, in 1883 (*Annales de Chimie et Physique*, xxviii. p. 480), undertook experiments to test the results obtained by Siljeström and Mendeléeff, but was unable to confirm them. His conclusion is, that for the lowest pressures measured (6.54 millim.) the differences were sometimes positive, sometimes negative; and that the necessary error of experiment was of an order of magnitude equal to that of the differences found. One of the main difficulties of observation was found in the diffraction of the walls of the manometer in which he measured the pressures to which the gases were exposed. He appears, however, to have been successful in overcoming this difficulty, by the use of polished plane surfaces; but it is noteworthy that a suspicion of this source of error does not appear to have occurred to either of the former experimenters. Amagat also states that the utmost limit of measurement is probably overestimated at 0.01 millim.; and indeed it is very difficult, if not impossible, to judge of the contact of two lines, the cross-wire of the cathetometer and the meniscus of the mercury in the gauge, to within such a minute distance. One of his criticisms of Mendeléeff's paper is worth quoting:—

“In M. Mendeléeff's experiments, a set of values of  $pv$  are obtained corresponding to a tolerably limited range of pressures; this would seem favourable to a knowledge of the direction in which these products alter; but it is necessary to guard against possible illusion in this matter.

“A constant cause of error may affect all these products; for as they deal with smaller and smaller values the effect will be more and more marked, and a regular variation may be conceived to exist, with no foundation in fact. Such an effect would be produced, for example, if the vacuum in the barometer were not absolute. It is certain, that whatever precautions be taken, this vacuum is not absolute; the effect of this is to diminish the real value of the pressures, that is to say, too small pressures are read: hence the value of  $p/p'$  is reduced, and since  $p$  is smaller than  $p'$ , the values of  $pv/p'v'$  are rendered too small; and as the error increases with reduction of pressure, they will ultimately be less than unity.”

Amagat proceeds to point out that even the vapour-pressure of mercury ceases to be negligible when a few hundredths of a millimetre cause the supposed deviation.

In 1886, C. Bohr (*Wied. Ann.* xxvii. p. 459) measured the pressures and volumes of rarefied oxygen. His conclusions are that at a temperature of  $11^{\circ}.4$  oxygen deviates from Boyle's law. For values of pressure greater than 0.7 millim.,  $(p + 0.109)v = k$ ; and for lower pressures,  $(p + 0.070)v = k$ . At 0.7 millim. therefore oxygen undergoes a sudden change

and becomes more compressible. This is a very strange conclusion, but it has been confirmed by our work.

In criticising Bohr's work, it is to be noted that he employed very wide tubes, one as barometer, the other to contain the rarefied gas. His method of reading was ingenious. Finding it impossible to read the level of the mercury in such wide tubes with accuracy, he placed in each a glass ball, and read its upper surface. The readings therefore appear to be very accurate. But the shape of the meniscus of mercury is different in a nearly perfect vacuum and in a vessel containing gas; it is always flatter in the vacuous tube. Hence the volume read was probably always too small; and increasingly smaller as the gas was more compressed. This would render the value of the product  $pv$  increasingly smaller, and necessitate the correction he applies. It would, however, not explain the breach of continuity which he observed.

Next in order of time comes a paper by F. Fuchs (Wied. Ann. xxxv. p. 430) in 1888. The lowest pressure which he measured was 248 millim.; but though he found deviations in the case of sulphur dioxide, hydrogen was normal.

In 1889, E. van der Ven carried out experiments by a method nearly identical with Siljeström's, but avoiding the possibility of cumulative errors which Siljeström's method involved. His conclusion is opposite to that of Mendeléeff and Siljeström; it is:—If a volume of air under low pressure, contained in a closed space, be doubled, it behaves as if its  $pv$  decreased with decrease of pressure. Thus he finds

At 62 millim. pressure,	$pv=0\cdot9873$ ,
At 31       "       "	$pv=0\cdot9811$ ,
At 16       "       "	$pv=0\cdot9740$ .

Van der Ven used iron cylinders with walls 6 millim. thick, and it is unlikely that any appreciable alteration in their volume would be caused by the differences in pressure which occur in his experiments. He appears also to have been careful about the temperature of the vessels. But the latter part of his paper is occupied with a discussion of the capillarity of his mercury-gauge; and it appears to us that a possible source of error lies here. For the height of the meniscus of mercury in a gauge is undoubtedly altered by the pressure of the gas in contact with it; and as the gas was rarefied, the apparent difference in height of the mercury in a narrow gauge like the one he employed would be influenced not merely by capillarity, but also by the form of the meniscus. We regard it as probable that the capillarity of mercury, like that of other liquids, is altered by the gas in

contact with it. In the empty, or comparatively empty part of the gauge, the capillary depression of the mercury is almost certainly not so great as in that limb exposed to gas; and the alteration of the pressure of the gas doubtless also alters the capillary depression. It would be worth while making this the subject of special experiments.

## 2. *Expansion of Gases at Constant Pressure, on Rise of Temperature.*

The last paper falling under our notice is one by G. Mehlender, published in 1892 (*Wied. Ann.* xlvii. p. 136). It deals with the thermal expansion of gases under reduced pressure. He concludes that the coefficient of expansion of air decreases from 0.003666 at 752 millim. to 0.0036594 at 232 millim., and again increases, with reduction of pressure, until at 6.6 millim. it amounts to 0.0037627; the turning-point of carbon dioxide is 76.2 millim.; with hydrogen there is no change in direction, but the coefficient increases from 0.0036504 at 764.5 millim. to 0.0037002 at 9.3 millim. These conclusions are opposed to those of Siljeström and Mendeléeff; for if the  $p_v$  increases, as stated by these authors, it is to be expected that the coefficient of expansion should decrease with decrease of pressure.

Before concluding this historical sketch, we feel it necessary to point out that it is exceedingly unlikely that these experimenters were dealing with pure gases. It is true that their apparatus were filled with comparatively pure gases; but they do not seem to have realized the fact that on reduction of pressure, gas different from that with which they were dealing comes off the walls of the containing vessel. When this is of glass, a very considerable amount of carbon dioxide is always evolved. At high pressures, of course, this would make a small difference, probably inappreciable; but as the pressure becomes lower, a gas like hydrogen will be partly removed, and its place taken by carbonic anhydride. One can never be certain of the purity of the gas measured unless its vacuum-tube spectrum is free from that of other gases.

Another source of error, small in itself, but possibly important when the small deviations which the experimenters are endeavouring to measure are taken into consideration, is of the nature of that pointed out by Lord Rayleigh as applying to Regnault's determination of the comparative weights of hydrogen, oxygen, and nitrogen. It is that the volume of a glass (and presumably of an iron) vessel is considerably diminished



if it be partially exhausted, owing to the external pressure of the atmosphere not being balanced by equal pressure in the interior. In Mendeléeff's experiments, for example, in which glass vessels were used, and in which the volume of the gas was ascertained by weighing the mercury run out of the vessel, it appears not unlikely that at low pressures the vessel contained less gas than at high pressures. The values of the products of pressure and volume,  $p_v$ , might really remain constant with decrease of pressure; but as he read pressure directly, and assumed a volume which was probably too great, he registered an increase. We are informed, however, by Professor Mendeléeff, that he introduced a correction for this possible deviation.

All the researches described aim at a direct measurement of pressure. Now there is a limit to the possibility of such measurement, and when the pressure is low, the readings necessarily involve considerable relative error, the extent of which is difficult, if not impossible, to gauge.

We have therefore adopted a different plan, which admits of the observation of the behaviour of gas at pressures much lower than most of those previously employed. We have met with difficulties, subsequently to be alluded to, which may vitiate the results for some gases; but for hydrogen the results are fairly trustworthy.

To describe the method in a few lines:—Two McLeod gauges are exhausted in communication with each other: one is heated to a known high temperature; and at the same instant, both are closed; after cooling the pressure is read in both. The readings afford data from which the expansion of the gas may be calculated.

#### DESCRIPTION OF THE APPARATUS.

The apparatus used for these experiments consisted essentially of two McLeod gauges placed side by side on a stand. These gauges were connected on the right to apparatus for exhausting them, and on the left to apparatus for admitting into them, when exhausted, measured quantities of the gas under examination.

The apparatus for exhausting shown on the right-hand side of the diagram consisted of a water-pump A worked by high-pressure water, and capable of giving a vacuum of 11 millim. of mercury.

The exhaustion of the apparatus was commenced by this pump and completed by the mercury-pump B. This mercury-pump discharged the gas taken out at each stroke into a

Torricellian vacuum which was sealed by two siphons *a* and *b*. By this means the gas in the large chamber of the pump suffered at most compression up to 4 millim. of mercury, so that the possibility of any considerable condensation of gas on the glass walls was eliminated, and each stroke of the pump removed as nearly as possible the theoretical quantity of gas.

For the preliminary exhaustion of the apparatus the water-pump A was connected with the top of the mercury-pump through the tubes and drying apparatus *αα*. When this preliminary exhaustion was complete, the mercury-pump was brought into action. The lowering and the raising of the mercury in the pump was brought about by alternately exhausting and filling with air the reservoir C which held the mercury. This could be done by hand: the exhausting by connecting it with the water-pump through the tube *β*, the admitting air by opening the tap *γ*; or, if preferred, by means of an automatic apparatus D through tubes *δδ*. In this apparatus a three-way tap was turned through 90° by a lever, from one side of which was hung a cup fitted with a curved siphon and from the other a counterpoise, water being run into the cup through a flexible tube. The working of this apparatus was quite constant, and was accurately timed so that if it were left working for a known time the number of the strokes of the pump could easily be calculated. The mercury-reservoir C was placed at such a height that under atmospheric pressure the mercury would run over the top siphon *a*, care being taken that the distance from the siphon *a* to the T-piece *c* was considerably less than 30 inches. In the pump used it was 24 inches.

The mercury in the two McLeod gauges E and F was regulated for purposes of reading by coarse and fine adjustment-screws G; there was also a connexion with a movable mercury-reservoir H. The tube I contained pentoxide of phosphorus for drying purposes, and J was a vacuum-tube. This last was absolutely necessary, as it otherwise would have been utterly impossible to ascertain whether or not the apparatus was full of the gas under examination.

The gas to be examined was admitted through the tap K out of the chamber L. By means of the apparatus shown in the drawing any amount, large or small, of the gas could be admitted. The chamber L could be exhausted by the connexion through the tap M to the water-pump; a wash-bottle N containing mercury was interposed to prevent any diffusion backwards of air or water-vapour into the gas.

The amount of gas admitted was regulated by means of

the siphon O which could be sealed by the mercury in the reservoir P. The mercury-level was adjusted by exhausting or filling with air the reservoir P in the same manner as with the reservoir C of the mercury-pump. The amount of gas admitted could, if desired, be measured in the gas volume-meter Q, which was designed on the model of the McLeod gauge. By means of this apparatus as small a quantity of gas as  $\frac{1}{50,000}$  of a cubic centimetre could be accurately measured and admitted.

The two gauges E and F were placed close together on the stand in order to bring them as much as possible under the same conditions of temperature and exhaustion, and were almost exactly of the same size. They consisted of a large volume-chamber (A) about 90 cub. centim. in capacity, with a pressure-tube (B) at the side and volume-tubes (C) and (D) at the top. The tube (B) was about  $\frac{1}{4}$  inch internal diameter; (C) consisted of a somewhat large capillary tubing, and (D) of a tube of very small bore. (C) and (D) were each about 250 millim. long. The volume and pressure tubes were accurately graduated in millimetres, the divisions on each exactly corresponding. The zero-points of the scales were placed at the top of (D) and at the corresponding place on (B). (B) was graduated 500 millim. below and 250 millim. above the zero-point. The total length of the volume-tube was of course 500 millim. A trap (E) was sealed below the chamber (A) in order to more accurately determine the volume of the gauge.

The calibration of the gauge was a most important point and was most carefully done. Every centimetre division on the volume-tube was taken as a reading-point, making fifty possible. At each of these points the capillary depression of the mercury had to be determined, *i. e.*, the difference in reading between the mercury levels in the pressure and volume tubes when both levels were under the same pressure. In order to measure these differences the extreme top of (D) was drawn out before a blowpipe to a fine point and the tip cut off. The gauge was then placed in an exactly similar position to that which it would occupy when finally fixed on the stand. Mercury was run in from the bottom and readings taken in the pressure-tube, with the mercury standing at each of the 50 reading-points on the volume-tube. After this had been done both with rising and falling mercury, the actual volumes corresponding to each of the 50 reading-points on the volume-tube measured from its upper end were determined. The tip of (D) was sealed, and accurately weighed

quantities of mercury were run in from a fine capillary tube which was pushed up (C) and (D). From the numbers thus obtained the volumes represented by each reading-point could easily be calculated. Lastly, the total volume of the gauge from the top of (D) to the trap (E) was found by weighing the gauge empty and then filled with mercury. From the data thus obtained a table was constructed giving the capillary corrections and volumes in cubic centimetres for each of the fifty reading-points, due allowance being made for the meniscus. A column was also added of the values of  $R$  for each graduation,  $R$  being the ratio of the total volume of the gauge to the small volume at each point, or  $\frac{V}{v}$ . This ratio is used in calculating the vacuum in millimetres in the apparatus from a reading of the gauge. McLeod has shown that if a pressure  $p$  be read, and  $R$  be the ratio at a point on the gauge, then the vacuum will be found from the expression  $\frac{p}{R}$ , or, if a second approximation be required, from

$$\frac{p + \frac{p}{R}}{R}.$$

The method of calculating the numbers read on the gauges was to multiply each pressure by each volume.

The following table shows the accuracy to be expected :—

$v'$ .	$c$ .	$v''$ .	$p'$ .	$p$ in mm.	$v$ in c.c.	$pv$ .
120	7.2	127.2	-11.0	116.2	.129	14.99
100	7.1	107.1	+31.9	139.0	.107	14.93
80	7.1	87.1	+86.9	174.0	.085	14.91
70	7.1	77.1	+122.6	199.7	.074	14.94
60	7.1	67.1	+166.5	233.6	.064	14.93

In the first column  $v'$  are given the reading-points on the gauge volume-tube. In the second column  $c$  are given the capillary corrections ; under  $v''$  the result of applying these corrections ( $v'' = v' \pm c$ ). Under  $p'$  the readings of pressure on the gauge,  $p$  the actual pressure exerted by the mercury on the measured gas  $p = v'' \pm p'$ , plus or minus according to whether the reading of  $p'$  is above or below the zero-point on

the pressure-tube (B). Then follow the volumes represented by the reading-points  $v'$ , and lastly the product of pressure and volume. In addition to this, if the original pressure in the apparatus before reading the gauge is over .1 millim. or thereabouts, this must be taken into account as the pressures found will be too small by this amount. The original pressure must therefore be found from the expression

$$\frac{p + \frac{p}{R}}{R}$$

as before shown and added to the values given in column headed  $p$  above.

When the calibration of the gauges was finished they were ready for use. In fitting up the apparatus it was absolutely necessary to seal all joints with a hand blowpipe so as to prevent any possibility of leakage. The tap K for the admission of the gas to be experimented on was an exceptionally good one of oblique bore. It was lubricated with gummy phosphoric acid, and though in constant use for over a year never once showed the faintest trace of any leak whatsoever.

During the experiments the mercury of the gas volume-metre Q was kept at a known point  $x$ , so that the volume of the apparatus to be exhausted was from the point  $x$  to the T-piece  $c$  of the mercury-pump, the tubes  $ee$ , together with the two gauges and the vacuum-tube J. The gauges when read had their volume-tubes jacketed with cold water; and fitted on gauge E on the diagram is shown the jacket-tube used in the experiments at high temperatures.

Whilst working with these gauges we noticed the following points amongst others. First, when the gauge is not in use, the mercury should be kept as close as practicable to the trap, for if it be kept some way below, the gas between the mercury and the trap will, on raising the mercury, inevitably be driven into the gauge and considerably disturb the accuracy of reading, even as much as seven per cent. error having occurred from this cause.

Secondly, the 'sticktion' of the mercury in the capillary tubes of the gauges is very apt to introduce large errors into the results, especially at high vacua, when the pressures and volumes to be read are very small. To overcome this difficulty the tubes were continually tapped before reading, and many readings were taken both after ascent and descent of the mercury. That this was necessary may be shown by the fact that the before-mentioned capillary corrections when measured

314 Mr. Baly and Dr. Ramsay on the Relations of Pressure, after ascent and descent of the mercury sometimes differed by as much as four millimetres.

It is also to be noted that the mercury must be raised very slowly, or gas will be trapped between the mercury and the glass. We also found it necessary to make the gauges of English lead-glass, as we found this to be the only glass that would stand the high temperature jackets without cracking.

#### EXPERIMENTS TO TEST THE ACCURACY OF THE MCLEOD GAUGE.

In order to determine once and for all the value of the McLeod gauge as a means of measuring vacua, some experiments were made with air. Many sets of readings were obtained, and they show the absolute failure of the gauge to measure vacua. It fails more and more as the vacuum improves. If the gauge had given trustworthy readings, the values of  $pv$  obtained at all reading-points should have been constant. We give here a set of values of  $pv$  measured at a moderate vacuum ( $p$  here refers to pressure in the gauge; not to the vacuum in the apparatus) :—

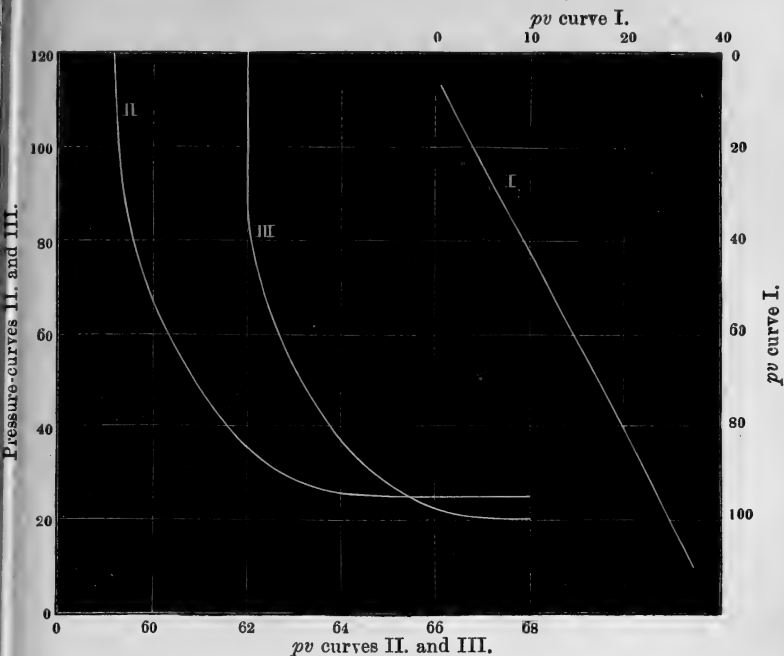
$p$ . millim.	$pv$ .
4.1	100
4.1	81.83
4.1	69.921
4.3	67.25
4.6	59.57
4.6	41.78
4.9	33.47
5.0	23.09
6.3	15.09
8.0	9.427

The other sets of values of  $pv$  obtained during this exhaustion varied from 100–95, 100–74, 100–65, 100–38, 100–18, 100–14. In each of these sets the first and highest  $pv$  is raised to 100, and all other values in that set raised in proportion.

The set of values of  $pv$  given above, decreasing from 100 to 9 was plotted against pressures and the curve (No. I.) drawn which gives the value of  $pv$  constant for minimum pressure somewhere about 270. This gives a vacuum of 9 millionths of an atmosphere, instead of .3 millionth.

But the curve, as thus drawn, is not correct, for the decrease in the values of  $pv$  is due to two causes. First, to the condensation of the gas on the glass as the pressure rises; and secondly, to the fact that Boyle's law does not hold good

for air at such low pressures. In addition to this, the surface of glass is uneven and not of uniform porosity. Two sets of



readings of the two gauges at the same vacuum were obtained with carbon dioxide. These two series were calculated for the same volume and were plotted against pressures. The two curves crossed at a point (Nos. II. & III.). Now this point, pressure and volume being the same, should be a point of equal surface, but it is very far from being so. We see, therefore, that equal pressures may condense quite different volumes of gas on two equal surfaces of glass; or, in other words, that two equal surfaces of glass may have quite different capabilities of absorbing a gas at a given pressure, owing apparently to want of uniform porosity. A curve drawn for a set of readings is, therefore, not to be depended upon. Indeed, with some gauges, the readings are so erratic that it is exceedingly difficult to draw a curve at all, and one of the gauges made for these experiments had actually to be discarded for this very reason. Such results as these put beyond a doubt the total worthlessness of the gauge as a means of measuring low pressures with air or with carbon dioxide.

With hydrogen, however, the case is different. After the apparatus was absolutely filled with hydrogen, the sets of

values of  $pv$  read on the gauges were constant, at least within the limits of experimental error.

We give a type of the series of readings we obtained :—

$p$ . millim.	$pv$ .
24·5	1·00
29·5	1·00
37·3	1·01
49·3	1·01
75·2	1·02
100·3	1·01
152·3	1·00

Many series of values of  $pv$  were obtained, and they prove that hydrogen expands quite normally between the limits 650 and 2·5 millim. of mercury pressure. We found it impossible with any accuracy to make readings in the gauges with a pressure smaller than 2·5 millim. These results also prove that hydrogen does not condense on a glass surface between these limits of pressure. By measuring the rate of exhaustion of an apparatus of known volume by a reservoir pump whose volume is also known, we found that hydrogen suffers no condensation on glass down to as low a pressure as ·000076 millim.

Let the volume of the apparatus be called  $V$  and the volume of the pump  $V'$ , then the pressure after a stroke of the pump will be  $\frac{V}{V+V'}$  times the pressure which existed before the stroke. This value may also be found experimentally by dividing the pressure after a stroke of the pump by the previously existing pressure. We have called this ratio the Factor of Exhaustion. It is evident that the constancy of this factor of exhaustion depends not on the expansion of the gas but on the possibility of condensed gas coming off the walls of the apparatus, in which case its value would increase. We made many series of measurements to obtain the factors of exhaustion, and found that they were quite constant and equal to theory down to the extreme limit of exhaustion.

We give here the results tabulated.

In the column headed ratio of gauge readings are given the ratios of the readings of the two gauges obtained at each measurement. As these, of course, ought to be constant, they may be looked upon as a measure of the experimental inaccuracies of the work, and may be used to correct the deviations observable in the values of the factors of exhaustion. In the last column are given the values of  $\frac{V}{V+V'}$



calculated from the apparatus and pump volumes. Any change in these indicates a new apparatus.

No. of Stroke.	Vacuum.	Ratio of Gauge Readings $\frac{E}{F}$	Factor of Exhaustion from gauge $E$ .	Factor of Exhaustion from gauge $F$ .	Theory. $\frac{V}{V+V'}$ .
1st Series *.					
Preliminary.	4 millim.	1·0359			
I. ....	2·6 „	1·080	·5497	·5273	·550
II. ....		1·0555	·5431	·5512	„
III. ....		1·0663	·5436	·5345	„
IV. ....		1·0256	·5254	·5462	„
2nd Series.					
Preliminary.	4·9 millim.	1·045			
I. ....		1·049	·5396	·5374	·540
II. ....		1·055	·5363	·5366	„
III. ....		1·0476	·5376	·5414	„
IV. ....		1·0475	·5430	·5432	„
V. ....		1·0495	·5351	·5394	„
VI. ....	·11 millim.	1·0444	·5463	·5515	„
		Mean ...	·5395	·5416	
3rd Series.					
Preliminary.	·07 millim.	1·040			
I. ....	·0401 „	1·032	·5553	·5592	·557
4th Series.					
Preliminary.	Very high vacuum.	1·0397			
I. ....		1·051	·6429	·6362	·560
II. ....		1·053	·5547	·5543	„
III. ....		1·042	·6165	·6232	„
5th Series.					
Preliminary.		1·0521			
I. ....	no connexion.	1·0494	·5374	·5388	·548
II. ....		1·054	·5413	·5386	„
III. ....		1·058			
IV. ....		1·0626	·5346	·5325	„
V. ....		1·060	·5389	·5401	„
VI. ....		1·0427	·5401	·5493	„
VII. ....		1·0368	·5395	·5426	„
VIII. ....		1·0366	·5412	·5412	„
IX. ....		1·0594	·5496	·5378	„
X. ....		1·083	·6289	·6462	„

\* In this series it had not been noticed that it was necessary to keep the mercury as close below the trap as possible, so as to avoid impelling gas into the gauge on raising the level of the mercury, in order to close it.

Table (continued).

No. of Stroke.	Vacuum.	Ratio of Gauge Readings $\frac{E}{F}$	Factor of Exhaustion from gauge E.	Factor of Exhaustion from gauge F.	Theory. $\frac{V}{V+V'}$
6th Series.					
Preliminary.		1·0549			
I. ....		1·0741	·5639	·5486	·548
II. ....	·004	1·094	·5681	·5630	"
III. ....	·0024	1·101	·6530	·6494	"
7th Series.					
I. ....	Very high vacuum.	.....	·5875	·5583	·590
II. ....		.....	·7362	·7670	"
III. ....		.....	·5857	·5912	"
IV. ....		.....	·5634	·6012	"
V. ....		.....	·6510	·5735	"

The last series vary a great deal owing to difficulties of reading, and also to the fact of the extremely high vacuum, pumping is performed by diffusion. The presence of mercury-vapour makes no difference in these experiments at all. When the mercury is raised in the gauges and the pressure on the gas rises, the mercury-vapour becomes condensed, and readings are only made of the hydrogen in the apparatus. When the mercury is lowered again, mercury-vapour doubtless mixes with the hydrogen till a state of equilibrium is reached, the percentage of mercury-vapour depending on the pressure. In working the pump also the presence of mercury-vapour has no effect, for the pump-chamber when the mercury falls is empty of hydrogen, and if there is any hydrogen in the apparatus it will diffuse in through the mercury-vapour. This explains how it is possible to exhaust an apparatus filled with hydrogen so far that the pressure of the gas left is considerably below the pressure of mercury-vapour, though of course the actual pressure in the apparatus is not below that of mercury-vapour, for as fast as the hydrogen diffuses out of the apparatus into the pump, its place is taken by more mercury-vapour. Apparently, however, there is a limit to this, for we were not able to take out any more hydrogen than is represented by the last reading of the table above. The pressure of hydrogen in the apparatus was about ·000076 millim., while the vapour-pressure of mercury is about ·0002 millim.

An interesting calculation may be made with this value. If the gas under examination were air and not hydrogen, then a great quantity of air would have condensed on the glass when the mercury was raised in the gauge to take the reading. If the curve (No. I.) were applied to this value, we should obtain the reading of the vacuum  $\cdot 0000022$  millim. This curve, however, was obtained for air at greater pressure than the above, and the condensation would be still greater at  $\cdot 000076$  millim., so that this is probably the highest vacuum that has yet been measured.

These results prove that hydrogen does not in any way condense on to a glass surface on rise of pressure, and that therefore in working a McLeod gauge with hydrogen all the gas in the gauge is measured and none lost by surface-condensation. The McLeod gauge is accordingly trustworthy to a certain extent when working with absolutely pure hydrogen.

With carbon dioxide, however, the case is different. Several series of factors of exhaustion were obtained with this gas, and it was found that they steadily increase in value as the exhaustion proceeds. This is owing to condensed carbon dioxide coming off the walls of the apparatus. It seems even possible to reach to a pressure which is equal to the "vapour-pressure" of the carbon dioxide which is condensed on the walls. For in a particular experiment the factors of exhaustion increased steadily till they reached  $\cdot 997$ , and 188 pumps more failed to make the slightest difference in the vacuum, as evidenced by the electric discharge in the vacuum-tube and by the gauge-readings. It would appear therefore that the pressure in the apparatus just equalled the pressure of the condensed carbon dioxide, and that as fast as the pressure was lowered by more pumping it was restored to its equilibrium by more carbon dioxide escaping from the pores of the containing walls. The vacuum was not very high, the *apparent* pressure being about one millionth of an atmosphere.

We found the converse of this when admitting measured volumes of carbon dioxide into a vacuum. In these experiments a gauge-reading was first taken and the *pv* calculated; then a known volume of carbon dioxide also calculated to *pv* was admitted. This last value multiplied by the ratio which the gauge volume bears to the rest of the apparatus will give the amount of carbon dioxide taken up by the gauge. This added to the previous value of *pv* read in the gauge ought to agree with the gauge-reading taken after the admission of the carbon dioxide. But we found that the measured *pv* was always smaller than that calculated. This shows therefore that some of the carbon dioxide condenses.

We give one series of measurements together with the values calculated from the known volume admitted:—

Calculated.	Found.
4.4	4.2
7.9	6.8
9.4	9.1
9.1	7.4
11.9	11.5
16.7	15.9
21.2	19.6

These results are a further proof that the McLeod gauge is of no value in determining the amount of rarefaction of carbon dioxide.

We also found it very easy to exhaust all hydrogen out of the apparatus if there were any condensed carbon dioxide on the containing walls. When the pump was started at about 10 millim. pressure, the spectrum of the gas in the vacuum-tube was only that of hydrogen. As the exhaustion proceeded the factor of exhaustion steadily increased while hydrogen slowly disappeared from the vacuum-tube and carbon dioxide became in evidence, till in a short time all the hydrogen had been pumped out and only carbon dioxide remained.

These facts may give an idea of the great difficulties we met with in filling the apparatus absolutely with hydrogen. This was a most lengthy and tedious operation. In spite of the fact that the apparatus used for the hydrogen experiments never had carbon dioxide put into it, the glass and the phosphorus pentoxide nevertheless contained great quantities of this gas condensed on them, the removal of which took a very long time. First of all the apparatus was exhausted as highly as possible and then the glass, especially the phosphorus-pentoxide tube, was raised to a high temperature with a Bunsen-burner, the exhaustion being kept very high in the meantime. Hydrogen was then admitted, and the apparatus again exhausted, the heating being still continued. This was repeated until no further carbon dioxide could be brought off the walls by the heating in the vacuum and until, after leaving it for a night, very highly exhausted, no spectrum of carbon dioxide was visible in the vacuum-tube when a current was passed. This process sometimes lasted a fortnight.

The foregoing results and the difficulties we met with in filling the apparatus with hydrogen emphasize our criticism on all previous work. For this fact of the condensation of carbon dioxide does not appear to have been noticed by previous experimenters. It would tend to make the read

pressure too high, for carbon dioxide, being evolved from the glass with decrease of pressure, would mix with the gas under experiment and increase the apparent pressure. It is probably the reason why the product of pressure and volume has so often been found to increase with reduction of pressure.

To measure the expansion of hydrogen below the pressure of 2·5 millim. the thermal method was adopted. One of the two gauges was jacketed at a known temperature, and the expansion of the gas thus determined. Readings were taken on both the gauges, and the ratio of the two sets of values of  $pv$  obtained. When the mercury is lowered in the gauges the gas expands, and though its expansion below 2·5 millim. may be abnormal, this ratio of the values of  $pv$  remains the same. One of the gauges is then jacketed and the other read. This reading multiplied by the ratio before obtained gives the  $pv$  of the hot gas in the other gauge. The hot gauge is then shut off and allowed to cool, when it is read. The ratio of the readings of the gauge when hot and when cold is equal to the ratio of the absolute temperatures. To give an idea of the accuracy of the method we quote an example :—

*Preliminary Readings to obtain the Gauge Ratio.*

Gauge E.	Gauge F.
<i>pv.</i>	<i>pv.</i>
376·2	395·1
375·4	394·6
376·3	394·5
376·5	395·0
375·6	394·8
Mean = 376·0	Mean = 394·8

$$\text{Ratio } \frac{F}{E} = 1·05.$$

Gauge F was then jacketed with aniline vapour. Barometer 764·9 at 0° C.

*Readings after jacket.*

E.	F.
<i>pv.</i>	<i>pv.</i>
379·84	247·60
379·71	247·41
380·11	247·94
379·78	248·25
379·17	247·71
Mean = 379·71	Mean = 247·782

Temperature = 12°·5 C.

When gauge F was hot the reading of gauge E was 379·71.

Therefore the reading of gauge F was  
 $379\cdot71 \times 1\cdot05 = 396\cdot80$ .

Boiling-point of aniline at barometric pressure 764·9 millim.  
 $= 184^{\circ}\cdot66$  C.

Therefore  $396\cdot80 : 247\cdot782 :: x + 184\cdot66 : x + 12\cdot5$  ;

$$\therefore x = 273\cdot741.$$

$$\therefore \text{Coefficient of expansion} = \frac{1}{273\cdot741}.$$

$$\text{Vacuum} = 3\cdot47 \text{ millim.}$$

In making these experiments the readings were taken at the same reading-points throughout the whole operation so as to ensure accuracy. It will be evident that the volumes represented by the divisions on the gauge do not influence the result, and provided that the whole calculation is made from readings at the same points, the volumes at these points may be given any value whatever. The accuracy of the experiment therefore does not depend in any way on the accuracy of the volumes at the reading-points, but only of the pressures, which were very carefully read to within 0·1 millim.

The following coefficients of expansion of hydrogen were obtained :—

(T=temperature of jacket ; t=temperature of reading.)

Pressure.		T.	t.
4·7 millim.	$\frac{1}{273\cdot5}$	184·66 C.	12·5 C.
3·47 „	$\frac{1}{273\cdot74}$	184·33	13·8
·25 „	$\frac{1}{276}$	132·32	14·7
·096 „	$\frac{1}{297}$	132·27	17·3
·077 „	$\frac{1}{300\cdot5}$	132·33	16·3

The purity of the hydrogen in these experiments was satisfactorily proved by both the constancy of the gauge-readings in each experiment and by the factor of exhaustion being equal to theory.

If the above results be plotted on a curve it shows that hydrogen expands quite normally till a pressure of ·4 millim. is reached, when its elasticity increases with further decrease of pressure. Many other experiments were made, with similar results.

Having thus satisfactorily proved that this method of determining the thermal expansion of hydrogen is capable of giving accurate results, we proceeded to apply it to determining the expansions of oxygen and nitrogen at reduced pressures.

In the case of oxygen the gas was made by heating permanganate of potassium, it was washed in caustic potash and dried by means of sulphuric acid and phosphorus pentoxide. Oxygen proved to be an exceptionally difficult gas to deal with, as it was found impossible to determine its purity by the electric discharge in the vacuum-tube, as the presence of dust or other combustible material led to the formation of carbon dioxide. This method therefore was of no use, and the purity of the oxygen was determined by the result obtained, as will be seen further on.

The coefficient of expansion of oxygen was found to be from very careful experiments :—

$$5.1 \text{ millim. } \frac{1}{261},$$

$$5.3 \quad ,, \quad \frac{1}{260},$$

$$4 \quad ,, \quad \frac{1}{262}.$$

These results are very fairly good, and being at such high pressures as 4 and 5 millim. may be said to demonstrate the absence of carbon dioxide, especially inasmuch as they give evidence of oxygen being too expansible while carbon dioxide is the opposite. Each of these results, too, was obtained after a fresh filling of the apparatus, which in each case was most carefully done. Therefore the proof that they are measurements of the expansion of pure oxygen may be regarded as conclusive. As the results next obtained gave evidence that with decrease of pressure the coefficient of expansion still further increased, and as on the slightest sign of presence of carbon dioxide the apparatus was most carefully filled again with oxygen, there is no doubt that the expansion of pure oxygen was in each case measured. The presence of a small quantity of carbon dioxide would materially alter the results, as the value of the coefficient of expansion of this gas is so small at the pressures here dealt with.

The anomaly in the expansion of oxygen, first noticed by Bohr, was brought very strikingly under our notice in working with oxygen. The vacuum was at one time 1.4 millim., when, on a stroke of the pump being taken, the remaining gas, now at a pressure of about .75 millim., behaved in a most extraordinary fashion. For example, the two gauges E and F,

which are of the same volume within  $\cdot 1$  per cent., gave values of  $pv$  which instead of being equal had a ratio to one another of 1 to 8·8. We give the values :—

Gauge E.		Gauge F.	
$p$ .	$pv$ .	$p$ .	$pv$ .
12·3	= 6·00	100	= 53·3
17·9	= 6·04	106·1	= 53·1
25·6	= 6·09	113·3	= 53·0
37·5	= 6·03	125	= 53·2
<hr/>		<hr/>	
6·04		53·15	

A large number of experiments were made, in which the gauges were continually opened and again closed and read, but the right ratio was not obtained until after 78 hours' rest. Then the readings in the gauge became normal, and an experiment was attempted to measure the coefficient of expansion, but the equilibrium of the gas was instantly disturbed, and the result came out about  $\frac{1}{1500}$ . When the apparatus was exhausted beyond this particular point, the behaviour of the gas became quite regular again, and two measurements of expansion were made. This same anomaly was met with again in subsequent experiments.

The coefficients of expansion of oxygen we obtained were as follows :—

		T.	t.
5·1	millim.	$\frac{1}{261}$	132·11
5·3	"	$\frac{1}{260}$	11
4·0	"	$\frac{1}{262}$	13
2·5	"	$\frac{1}{251}$	9·4
	"	$\frac{1}{250}$	11·5
1·4	"	$\frac{1}{233}$	10·9
·083	"	$\frac{1}{244}$	9·1
·07	"	$\frac{1}{240}$	11

It will be seen, therefore, that the coefficient of expansion of oxygen decreases with decrease of pressure. Having a value of about  $\frac{1}{261}$  at 5 millim., it increases steadily to where the change takes place. At a rarefaction greater than at this point, the value of the coefficient is again smaller, but it still appears to increase with further diminution of pressure.

It is difficult to account for the abnormal behaviour of oxygen as regards distribution in the gauges at a pressure of



0.75 millim. The only possible explanation appears to be that the temperatures of the two gauges must have differed to a small extent, and that the smallest difference in temperature produces quite an unusual disturbance in equilibrium.

Nitrogen was next experimented upon. The gas was prepared by absorbing the oxygen from air, first as far as possible by means of pyrogallate of potassium, and then by passing it over red-hot copper-gauze.

The experiments were carried out in the usual way, and there was no special difficulty connected with the filling of the apparatus with the gas.

The great difficulty in working with nitrogen was that experienced in obtaining satisfactory and concordant results in measurement of the ratio between the gauge-readings preliminary to the jacketing. This difficulty increased as the vacuum improved, and it was found impossible to obtain results of any value whatever at a less pressure than .6 millim. The readings for the ratio were always taken with the utmost care, but in spite of this ratios sometimes differed amongst themselves as much as 2 per cent., which means a difference of 9 or more per cent. in the values of the coefficient of expansion.

The numbers obtained were as follows:—

Pressure.	T.	t.
5.3 $\frac{1}{304.}$	132.55	8.8
4.97 $\frac{1}{303.8.}$	132.16	9
3 $\frac{1}{301.6.}$	132.42	8.5
1.1 $\frac{1}{304.}$	131.7	14
.8 $\frac{1}{331.}$	131.6	12.5
.6 $\left\{ \begin{array}{l} \frac{1}{355.} \\ \frac{1}{343.5.} \end{array} \right\}$	132.1	11.5
.6 $\left\{ \begin{array}{l} \frac{1}{377.} \\ \frac{1}{323.} \end{array} \right\}$	132.1	13
.6 $\left\{ \begin{array}{l} \frac{1}{301.} \\ \frac{1}{327.} \end{array} \right\}$	131.6	13
.6 $\left\{ \begin{array}{l} \frac{1}{371.} \\ \frac{1}{343.} \end{array} \right\}$	132.2	13

Mean of eight  $\frac{1}{342.56}$  at .6 millim.

These last values of the coefficient of expansion are in four sets, each set being the result of an entire fresh filling of the

apparatus with nitrogen. The two values in each set have been calculated with the two extreme values of the gauge ratio that have been obtained during the experiments at this pressure  $\cdot 6$  millim. Though the results are not good, they nevertheless show that the coefficient of expansion of nitrogen for one degree Centigrade decreases with decrease of pressure.

To sum up the results :—(1) The coefficient of expansion of hydrogen with temperature decreases as pressure is lowered. It is normal down to a pressure of  $0\cdot 1$  millim. (2) The coefficient of expansion of oxygen is greater than the normal one, being  $1/262$  instead of  $1/273$  ; it increases with decrease of pressure to  $1/233$  at  $1\cdot 4$  millim. pressure ; at  $0\cdot 7$  millim. pressure it is erratic ; but at lower pressures it again becomes more constant, still showing, however, a tendency to increase as pressure is decreased. (3) With nitrogen the coefficient of expansion is lower than the normal ( $1/304$ ) at pressures between  $5$  and  $1$  millim. ; at lower pressures, like that of hydrogen, its coefficient of expansion decreases ; that is the gas becomes more elastic. (4) So far as it was possible to experiment with carbon dioxide, its behaviour appears to resemble that of hydrogen and nitrogen ; but owing to the tendency which it has to condense and cling to the gauge, trustworthy measurements were impossible to attain. These results corroborate those of Mendeléeff and Siljeström, although they are deduced from thermal expansion, while theirs were deduced from the compressibility of the gas. And Bohr's results as regards the abnormality of oxygen were also confirmed, although likewise by a different method.

If it may be taken for granted, then, that the rate of expansion of gases decreases with decrease of pressure, it is necessary to inquire why this is the case. From the point of view of the kinetic theory, pressure is caused by impacts on the walls of the containing vessel of the molecules which it contains, due to their translational motion. The internal motion does not give rise to pressure. If, on communicating to a gas energy, by raising its temperature, it does not respond by a sufficient rise of pressure, it appears to us that the conclusion is inevitable that its internal energy is increased to a greater than usual extent compared with its translational energy. It is perhaps idle to speculate on the extreme final state of rarefaction ; but if this diminished rate of expansion were to continue to increase with tenuity, a point might conceivably be reached where all received energy would result in internal motion. Can this be the cause, or one cause, of phosphorescence in high vacua ?

In his *Allgemeine Chemie*, second edition, vol. ii. p. 32,

Ostwald treats of the limiting phenomena of volume-energy. He suggests that if it be conceivable that the volume of a gas is increased indefinitely, the volume-energy obtainable from a gas would also increase infinitely, involving the consequence that from a finite quantity of gas an infinite amount of heat of constant temperature could be converted into kinetic energy. He therefore suggests that at some very great, yet finite volume, the pressure should become zero, and the gas should therefore refuse to increase its volume. Instead of the expression for

Boyle's law,  $pv=c$ ,  $(p+k)v=c$ , where  $k=\frac{c}{v_{\max}}$ , i. e. at a volume where  $p=0$ . Such a supposition would place an upper limit to the atmosphere. Similar considerations are also applied by him to gravitational energy.

The abnormal behaviour of oxygen is, if not more, at least equally difficult to explain. Some profound change must take place suddenly at the pressure 0.7 millim. Whether this change is of the nature of dissociation or not, cannot readily be determined; but the spectra of oxygen appear to show that it is able to exist in several modifications at low pressures.

The work described appears to us very incomplete; yet it has not been for want of time and trouble spent on it. The experiments are of extreme difficulty, and it has taken close on two years to arrive at the results chronicled, imperfect as they are. We are, however, somewhat cheered to learn that the experience of Professor Mendeléeff has in this respect been like ours; that a short column of figures can express the results of the labour of years.

University College, London,  
20th May, 1894.

### XXXVI. *Notices respecting New Books.*

*The Steam-Engine and other Heat-Engines.* By J. A. EWING, M.A., B.Sc., F.R.S., M. Inst. C.E. Cambridge: at the University Press.

**P**ROFESSOR EWING'S article on the Steam-Engine in the *Encyclopedia Britannica* reads like a set of most excellent lecture-notes. In the present book the *Encyclopedia* article may easily be recognized; but if we may dare to say so, it is like recognizing the features and manners of a clever Scotch medical student in an accomplished and experienced London physician.

Although short for such a great subject, its style is polished; and because the author has not only studied his subject, but also his students, the book reads very easily. Only in a very few places does there seem to be any of that useless mathematics with

which many modern engineering books are stuffed. On the other hand, it would be easy to point out places in which a somewhat fuller treatment of the subject would have been an improvement. Every statement will stand examination, there being nothing slipshod either in the author's knowledge of the principles of science, or in his application of these principles to the exceedingly complicated phenomena with which the practical engineer has to deal. It is just possible that exception might be taken to the author's way of speaking of the absolute zero of temperature and of absolute temperature, as if we knew its scale at very low temperatures. In this, if he is in error, he errs with 99 per cent. of the writers of books.

The book is illustrated with many woodcuts, and gives a good general idea of the most recent engineering practice; but the author has very rightly left out such illustrations and descriptions of mere details as are far better studied in shops and in drawing-offices and their usual books of reference.

We are glad to see a clear description of the uses of the temperature-entropy diagrams which Mr. Macfarlane Gray has for so long been endeavouring to make engineers understand. It is certain that no educated engineer who practises with it for an hour will ever dispense with its help in his study of a heat-engine. For the study of steam-engines we have a curve whose vertical ordinate is  $\theta$  the temperature and abscissa  $\phi$  the entropy of 1 lb. of water, and we have another curve for 1 lb. of dry saturated steam. An adiabatic line in this diagram is a vertical straight line and areas represent amounts of energy as heat or work. Assuming no standing water in the cylinder, or assuming that the whole mass is at the same temperature, and given the feed-water per stroke as well as the indicator-diagram, it is astonishing how much information as to rate of reception or loss of heat and condensation or vaporization is given easily by the  $\theta, \phi$  diagram.

That the alternate heating and cooling of the cylinder is the great source of waste in a steam-engine was clearly pointed out by Watt. That high temperature (and therefore pressure) of the entering steam leads to greater efficiency has been more or less correctly known since the time of Carnot. But these two principles are antagonistic, because the second necessitates great expansion, and this implies great range of temperature, and hence each of these principles has been learnt and forgotten again, eulogized and condemned, several times during the last eighty years. The valuable work of Rankine, which might have been of enormous use to the practical men, could not be recognized by them because the actual waste in well-made engines was unaccounted for by his theories; yet Clarke's experiments were made in 1855 and Isherwood's in 1863. Just before Rankine's death he was beginning to take the missing water into account, as is evident in his memoir of John Elder. Elder, in a paper read before the United Service Institution in 1866, showed that it was advantageous to employ a compound engine with two cylinders when expanding steam to five

times its volume, and one with three cylinders for successive expansion to ten times the volume.

We read the history of the steam-engine with much humility. It is a history of the work of theorists without practical knowledge and of practitioners without theoretical knowledge, entirely out of sympathy with one another because each side of them could see that the other side was wrong. This is even now only slowly being replaced by a better state of things, a number of young practitioners being fairly well equipped with scientific knowledge; but the prejudices of the "rule of thumb" engineer are not by any means dead; and many of his sneers at the so-called theorists are not altogether undeserved.

The solution of the problem which is now generally adopted is that of expanding the steam successively in a series of cylinders so that the range of temperature in each shall be small, and to shorten the periodic time to take advantage of a well-known fact in heat-conduction—that the amount of heat entering the metal when its skin is higher in temperature than the portions inside or leaving the metal when the skin is lower in temperature, say, during a half period, is inversely proportional to the square root of this periodic time. The phenomena are very complicated, and we are only gradually getting to understand how to make experiments. There can be no doubt that the film of water which adheres to the metal surfaces performs a most important function; for no ordinary emissivity of surface will account for the great rapidity with which the entering steam gives up its heat; but it can be explained by the evaporation or condensation of water and steam at their surface of separation. If we take it that the whole of this water is always at the temperature of the steam and consider the metal to be nonconducting, the work per stroke will now be proportional to the amount of water present, and will be independent of the periodic time. Such experimental results as we have seem to indicate that the loss per stroke is not inversely proportional to the square root of the periodic time, but it is not independent of the periodic time.

If the water alone were operative, it is an interesting inquiry, Ought not the amount of water present to go on increasing? The calculation is more difficult than it seems at first sight. How much steam will condense when it enters the cylinder? How much will condense in the adiabatic expansion? These are easy enough, although the first is an irreversible process; but in the irreversible phenomenon of release to the condenser there is a step-by-step approximate integration to be performed, which is very tedious; we know from actual experiment that the average mathematical physicist needs ten days to find out the difficulty of this problem. It is difficult to see why, as a rule, in all engines there is so little condensation or vaporization during the expansion when there is such enormous condensation during the admission, and yet the piston is continually exposing fresh cold surfaces. Condensation is probably going on at these cold surfaces, and nearly equal

vaporization is going on from the now warmer surfaces. It is just possible that condensation and vaporization due to such causes as adiabatic expansion and free rushes of steam do not affect the amount of water deposited on the metal surfaces; they only affect the quantity of finely divided cloud.

All engineers are now convinced that it is important to diminish the amount of water present before admission; and three methods have been adopted for this which are all effective. One which was tried about thirty years ago, and abandoned for insufficient reasons, was to superheat the steam: this will probably be tried again. The second was the invention of Watt: it is to heat the cylinder from the outside by a steam-jacket, or a flue-jacket, or a gasflame-jacket. Among all the experiments carefully carried out during the last twenty years to discover whether the waste of steam in the jacket was less than the saving effected by its use, we think that there is not one in which the use of the jacket did not lead to economy. The economy effected by the use of the jacket is very much more noticeable in cylinders, which without it were very wasteful.

The third plan is that of facilitating the drainage of the cylinder. We may not be able to drain off the water-film which adheres to all the inner surface of the cylinder, but we can prevent the collection of water in pockets; and there can be no doubt that it is to this that the engine of the late Mr. Williams owes most of its efficiency.

We do not know that there has yet been much of an attempt to hinder the condensation by the use of paint or varnish or a lubricator; but a very much more promising plan, which has not yet been tried, and which might be of special use in non-condensing engines, is that of mixing with the steam air or some vapour whose condensing temperature is much less than that of steam. The experiments of Prof. Osborne Reynolds about twenty years ago showed that a comparatively small amount of air very greatly retarded the condensation of steam when suddenly admitted to a cold vessel. In this connexion it will be interesting to see the results of some experiments of which we have heard in which a cylinder is, in alternate strokes, that of a steam-engine and that of a gas-engine.

The use of steam-engines to drive electric-lighting dynamo-machines with loads which vary greatly during the twenty-four hours, and especially in places where space is valuable, has given prominence to the study of the behaviour of engines in which nothing varies but the initial pressure of the steam. Mr. Williams found that in any trial with very varying loads, when plotting "water per hour  $W$ " and the indicated horse-power  $H$ , his points lay in a straight line. The result is rather striking, so striking, indeed, that " $W$  a linear function of  $H$ " has already been called "the Williams law." Knowing, as we do, that the missing heat is proportional to the range of temperature, and using the Rankine method of calculation from Hypothetical Diagrams, it is easy to

see that, mainly on account of the volume of 1 lb. of steam being nearly inversely proportional to the pressure, the curve connecting  $W$  and  $H$  is very nearly straight within the limits of such ordinary pressures as are used in engines. It is unfortunate that there are engineers who forget that the law is an empirical one, and who are already speculating on the meaning of the Williams law when the  $H$  is negative. The useful horse-power given out by the crank-shaft and the electrical horse-power given out by the driven dynamos are known to be linear functions of the indicated horse-power  $H$  with considerable accuracy; and hence  $W$  is a linear function of each of these powers also.

Any general law like this which simplifies calculations is of enormous use to practical men. It is of importance to note that, from theoretical considerations, it is probably to be relied upon as being generally true; for the practical man is very provincial, and he is a little too apt to assume a general law from his own restricted experience.

On the subject of gas- and oil-engines Prof. Ewing has given just enough to make us wish that he had devoted three times the space to it. Except in the noisy Otto-Langen of 1866—now seldom seen—no one except Mr. Atkinson has made a serious attempt to get rid of the enormous waste due to the water-jacket. In the usual working of gas- or oil-engines the water-jacket carries off just half of the total available energy of the gas or oil. The average velocity with which each part of a cycle is performed is probably now as high as it conveniently can be made to be, consistently with certainty that each operation shall be properly performed. But after ignition of the charge, if there is not too much inert matter present, and if the mixture of air and gas was sufficiently intimate, we have no reason to believe that four times the present velocity in the expansion-stroke would do any harm, whereas the cooling due to such a rapid expansion would probably do away, almost altogether, with the necessity for a water-jacket. It is known, indeed, that exceedingly rapid cooling of red-hot, and therefore dissociated, carbonic acid allows it to remain partially dissociated at the lower temperature, like the carbon in steel (possibly); but experiment would easily settle the rate of expansion which produced maximum economy.

Besides Mr. Atkinson's method of giving rapid expansion, we might effect the same object by the use of a springy attachment of the fly-wheel to the crank-shaft. It is unfortunately the difficulty of balancing reciprocating masses which now troubles the gas-engine maker, as it troubles also the steam-engine manufacturer; and it is possible that the large gas-engine of the future will consist of a pump pumping a mixture of air and gas or oil at great pressure into a white-hot firebrick chamber from which it will issue, driving a turbine on the Parson's steam-turbine principle.

The steam-engine constructor seems rather to dislike statements of the actual thermodynamic efficiency of his engines. Rightly enough, his standard of comparison is a perfect steam-engine

working with the same limits of temperature. But even here he takes as his lower limit of temperature the usual temperature of the exhaust in the actual steam-engines, and not the lowest temperature possible, say, the average atmosphere temperature; and in the case of the condensing-engine he makes his standard defective in another way by limiting the maximum volume of the standard engine's cylinder.

Instead of speaking of pounds of coal per hour per indicated horse-power, he prefers to speak of pounds of steam; and the manufacturer of our generation is rightly proud to have reduced this from numbers greater than 30 lb. of steam per hour per indicated horse-power to numbers less than 14. To those of us who lament the waste of our fuel, it is more instructive to consider the *absolute* efficiency of the steam-engine. It is only the very largest and best of steam-engines which can be said, even by their constructors, to give, during an exceptionally well-stoked trial, one *actual* horse-power for 1.6 lb. of coal per hour. This means that the energy utilized is only about 17 or 18 per cent. of the supply in the very largest and best of steam-engines! There is some comfort in the thought that even in small gas-engines 1 actual horse-power is obtained from very little more than 1 lb. of anthracite per hour when Dowson gas is used. In the animal machine over 90 per cent. of the supply of energy in the fuel may be converted into useful mechanical work. The man who first shows us how, in a small space and without excessive cost of plant, we can convert the chemical energy of coal and air into electrical energy, as zinc is burned in a voltaic cell, will be the greatest benefactor of his race—if he only comes soon enough.

JOHN PERRY.

### XXXVII. *Intelligence and Miscellaneous Articles.*

HEAT OF DISSOCIATION ACCORDING TO THE ELECTROCHEMICAL THEORY. BY H. EBERT.

EVERY stage in the development of chemistry can show experiments made to account for the forces which hold together the atoms in compound bodies. In immediate connexion with Kekulé's doctrine of Valency, von Helmholtz, on the basis of Faraday's law of Electrolysis, was the first to show in the case of electrolytes, that each valency must be considered charged with a minimum quantity of electricity, the "valency-charge," which like an electrical atom is no longer divisible\*, so that chemical affinities

\* That for electricity also there are minimal quantities which can be no longer divided, and which are associated with the smallest particles of ponderable masses, may be differently expressed. Let  $e$  be this elementary quantity, and  $X$ ,  $Y$ , and  $Z$  the components of the forces exerted by it, then

$$e = -1/4\pi(\partial X/\partial x + \partial Y/\partial y + \partial Z/\partial z).$$

The expression within the brackets is, however, nothing more than the



are in fact determined by the electrostatical situation of these elementary charges which attach to corporeal atoms of various fluids. According to this theory, the work of dissociation which must be expended in order to decompose an electrically-neutral molecule into its constituents which are charged with electricities of opposite polarity, must be identical with the work to be expended in removing the electrical *valency-charges* from their actual distances in the molecule to such distances that we can regard the molecules as dissociated. The heat of dissociation must then be partially or wholly equivalent to *electrical work*. We shall see that this is actually the case, that the heat of dissociation is already entirely consumed in overcoming the electrical attractions of the valency-charges, so that, compared with the electrical, purely chemical forces altogether recede.

If the valency-charges  $+e$  and  $-e$  at the position of valency adhere each to an atom united to form an electrically neutral molecule, they would attract electrostatically at the distance  $r$  with the force  $f = -e^2/r^2$  dynes.

How these elementary quantities are arranged in the atoms we are ignorant. From the fact of radiation, which we may refer to vibrations of the valency-charges, we must conclude that they must oscillate about certain mean positions, yet nothing exact is known as to the distance of these centres of oscillation in the molecule.

As a first approximation we may regard the atoms as spheres which lie close to each other in the molecule. The diameter  $d$  of what is called the sphere of action of the molecule is then of the order of the sum of the diameters of the spheres. The simplest assumption which we could make as to the oscillations of the valency-charges would be that we regard them as taking place in each atom symmetrically about the centre. The mean reciprocal distance of the valency-charges in the non-dissociated molecule is then  $= \frac{1}{2}d$ . Accordingly, in order to move the valency-charges from their distance from each other in the molecule, to such a distance that they no longer act on each other, the work required for each molecule would be  $a = -e^2/(\frac{1}{2}d)$  ergs, and for the molecular weight the work  $A = -ze^2/(\frac{1}{2}d)$  ergs,  $z$  being the number of molecules.

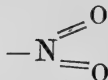
If, therefore, in comparison with the electrical forces those of

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“convergence of electrical lines of force” (Maxwell, Treatise, i. § 25, p. 29, 2nd edition; compare also Heaviside, Electrical Papers, i. p. 210, 1892). So that we may also say, the convergence of electrical rays of force towards an atom of ponderable matter cannot sink below a certain limit. According to this the existence of electrical elementary quantities is closely connected with the *geometrical* properties of our space and its being filled with matter. By resting on definite mechanical representations further reasons may be adduced: thus, for instance, tubes of force are identified with vortex threads of the æther, as in some mechanical theories of the electrical field. Such threads can return to themselves, or may end in the corporeal atoms in the æther. But as they must have a definite cross section, only a limited number can terminate on a smallest corporeal particle.

another kind, such as chemical affinity, and the gravitating forces of ponderable masses are quite insignificant, the work of dissociation must be quite defined by valency-charge, number of molecules in the molecular weight, and molecular diameter. As regards the work of gravitation von Helmholtz has shown \* that it quite disappears in comparison with the electrical work, since the electrical forces of the charges are many million times greater than the gravitating forces of the corresponding material carriers. As it will be seen that the work of dissociation calculated from the magnitudes mentioned agrees in the order of their magnitude with those determined experimentally, specially chemical forces can play no great part in comparison with electrical forces, and we must conclude that chemical affinity is essentially an electrical property of the smallest particles.

M. F. Richarz † has formerly shown that in the case of nitric tetroxide we arrive at plausible values for the sphere of action of the molecules, if we consider the work needed for dissociation of  $\text{N}_2\text{O}_4$  into  $2\text{NO}_2$  as an electrical one done against the attractions of the elementary charges; in this he assumes that such elementary charges attach to the free valency of the monovalent group



It must be of interest to make such a calculation for the important case of an elementary gas. In this respect hydrogen and iodine vapour have the recommendation that we have definite values for the heat of dissociation. According to Helmholtz's electrochemical theory in the case of hydrogen the two atoms hold together in the molecule, because one of them possesses at its position of valency a positive quantum of electricity, which it would have for example in an electrolyte; the other, on the contrary, has had to change its positive charge, in an electrolytic process for instance, for an equal negative charge, and is thus negatively charged. Hence the hydrogen molecule is externally electrically neutral. Iodine is analogous. The conception of a molecule consisting of a positive and a negative atom has been successfully applied by MM. W. Giese, A. Schuster, J. J. Thomson, Elster and Geitel, &c., to explain a series of phenomena of gas-discharges.

We have experimental data about the dissociation of hydrogen. In 1880 E. Wiedemann, in his experiments on the thermal and optical deportment of gases under the influence of electrical charges, has determined the heat  $W$  necessary to resolve the molecules of hydrogen which show the band-spectrum into the individual atoms, which then show the well-known line-spectrum.

\* H. v. Helmholtz, *Vorträge und Reden*, ii. p. 317 (1884).

† *Sitzungsberichte der Niederrhein Gesellschaft zu Bonn*, Jan. 12, 1891; *Verhandl. der Phys. Gesellschaft zu Berlin*, June 26, 1891, p. 73.

This he found to be 128,300 gramme-calories per gramme of hydrogen. This number must be regarded as an upper limiting value for the heat of dissociation of  $H_2$ , for in it that quantity of heat is contained which must be used to bring the hydrogen to the boundary of dissociation. Yet this value is in any case very near the true heat of dissociation.

Hence direct calorimetrical measurements give for hydrogen  $W_{H_2} \leq 1283 \times 10^5$  cal., or for a molecular weight of hydrogen  $W_{H_2} \leq 2566 \times 10^5$  cal.

In the case of iodine vapour Boltzmann\*, from the course of the dissociation with the temperature according to the observations of Meir and J. M. Crafts, has calculated the heat of dissociation at  $y=1125$  calories per gramme. Hence, in order to dissociate a weight equal to the molecular weight 253.6 of  $I_2$ , there are required  $2853 \times 10^4$  calories.

This number, as will be seen, is of the order of that obtained for hydrogen by M. E. Wiedemann by a totally different method. That it is smaller agrees with the fact that iodine vapour is dissociated at temperatures at which this is not the case with hydrogen, that the band-spectrum of iodine vapour is very difficult to obtain, and so forth.

In ergs, Wiedemann's measurements give for hydrogen the work of dissociation

$$A_H \leq 1.1 \times 10^{13} \text{ ergs.}$$

The theoretical reasonings of Boltzmann give for the work of dissociation of iodine,

$$A_I = 1.2 \times 10^{12} \text{ ergs.}$$

All other data required for making the calculation are furnished by electrolysis and the kinetic theory of gases.

From the most recent determinations of F. and W. Kohlrausch on the volume of detonating gas liberated by 1 ampere in a second, Richarz (*vide antea*) calculated the magnitude of the elementary quantum of electricity  $e = 1.29 \times 10^{-10}$  C.G.S. I myself† found by a totally different way the assumption that the energy of radiation of a luminous vapour depends on electrical vibrations of these valency-charges  $e = 0.14 \times 10^{-10}$  C.G.S.; a number, therefore, which in the order of magnitude is quite comparable with the first, and therefore conversely justifies the assumption in question.

The kinetic theory of gases gives for the molecular diameter  $d = 10^{-8}$  cm., and for the number of hydrogen molecules in the unit of weight  $6.7 \times 10^{23}$ ; in the molecular weight of any gas or vapour there are thus  $z = 1.3 \times 10^{20}$  molecules.

If these values, taking Richarz's for  $e$ , be placed in the above formula, we get

$$A = 4.3 \times 10^{12} \text{ ergs.}$$

\* *Wiener Berichte*, 1883, p. 861.

† H. Ebert, *Wied. Ann.* xlix. p. 651 (1893).

This value is quite of the order of the value above given for hydrogen  $A_H \leq 1.1 \times 10^{13}$ , and that for iodine-vapour  $A_I = 1.2 \times 10^{12}$  ergs; it is indeed somewhat greater than the latter.

From this it results that *the whole work required for the dissociation of hydrogen and iodine molecules is used in overcoming the purely electrical attraction forces of the valency-charges.*

That this heat of dissociation is so completely spent in electrical work shows, in agreement with many other facts, *that the forces of chemical affinity are essentially of an electrical character; that the electrostatical forces which the charges exert on each other at the positions of valency are "by far the most powerful among the forces exerted among the atoms;"* and that in H. v. Helmholtz's 'Faraday Lectures,' *particular possible chemical forces of the charged atoms can be but infinitely small in comparison with electrical forces.* This seems of great importance for the theory of chemical forces in general.—Wiedemann's *Annalen*, No. 10, 1893.

#### ALTERATIONS OF THE ELECTRICAL RESISTANCE OF AQUEOUS SOLUTIONS AND OF GALVANIC POLARIZATION WITH PRESSURE. BY BRUNO PIESCH.

A large series of liquids were investigated, both acids and solutions of salts. The method of measurement was such that the resistance and the polarization could be determined simultaneously.

The great pressure was produced by a Cailletet's apparatus, which held up to 600 atmospheres. The resistance-vessels consisted of a combination of glass tubes, which could be connected externally by means of ebonite cemented in the metal cap, which was firmly screwed in the iron cylinder.

The measurements gave the following results:—

Change of pressure produces a change of resistance, which decreased in all cases with increase in the pressure. No regular influence of concentration could be observed, but with most substances the variations of a less concentrated solution were greater than of a concentrated solution.

As the pressures increased the decreases of resistance were less. Polarization also showed a change of value with higher pressure. These, however, are for the most part small. An increase of polarization with the pressure was in general observed. The irregularities here shown were greater than with the measurements of resistance.

In conclusion, a solution of  $NH_4NO_2$  in alcohol was investigated, and alterations in the same direction were here met with.—*Wiener Berichte*, May 25, 1894.

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OCTOBER 1894.

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XXXVIII. *Fixed-Arm Spectroscopes.*

By FRANK L. O. WADSWORTH\*.

[Plates VIII.-X.]

IN prismatic spectroscopes and spectrometers of the usual construction it is necessary, in order to observe different portions of the spectrum under the same conditions, to vary the angle between the axes of the observing and collimating telescopes by the rotation of the arm which carries one of these telescopes about an axis parallel to the refracting edge of the prism. Usually the arm which carries the slit and the collimating-lens is fixed, and that carrying the observing telescope is movable; but sometimes the apparatus which it is necessary to carry on the observing arm is so massive, or else requires such a degree of stability, that it becomes necessary to fix it in position and make the slit-arm the movable one. Then difficulties are at once encountered in the illumination of the slit, if a fixed source of light such as the sun or a star is under examination. Even if terrestrial sources be employed, it is oftentimes extremely undesirable to have a complicated system of collimator, slit, condenser, and source of light, swinging about on a long arm, and in particular cases such an arrangement is absolutely inadmissible. In such cases where both arms of the spectroscope are necessarily fixed, we

\* Communicated by the Author.

may easily bring different parts of the spectral field to the cross wires of the observing telescope by a rotation of the prism alone ; but in none of the usual forms without violating the usual condition imposed in spectroscopic work, viz., that the prism shall always be in minimum deviation for the central ray in the field.

Heretofore the only forms of "fixed-arm" spectroscopes which fulfil the latter condition have been of the Littrow type, in which the ray is, by a system of reflecting surfaces, made to traverse the prism twice in opposite directions, and to emerge finally in a direction parallel but reversed in direction to that in which it entered.

The original form and the various modifications of this instrument have been already described\*. While they fulfil the condition of bringing any part of the spectral field into the field of the observing telescope without changing the angle between the latter and the collimator, there are certain objections to all of them. The most serious objection to the original form, that of a general illumination of the field, has been simply and successfully overcome in the manner already pointed out by the author †, but the second objection, that of a close proximity of the slit to the observing eyepiece, remains. Young's and Browning's modifications overcome this latter as well as the former difficulty ; but they are both complicated and expensive, necessitating as they do the use of at least three reflecting-surfaces and two independent telescopes, in addition to the usual prisms. Moreover, with all instruments of this general type, it is necessary for the beam of light to pass twice through the prism or train of prisms, and this, where brightness is of more importance than large dispersion, as with very faint sources of light for example, is a disadvantage. For these reasons I have thought it would be of interest to describe some simpler forms of "fixed-arm" spectroscopes, which I have recently devised and used, and in which the usual arrangement of parts may be preserved, viz., a separate collimating and observing telescope, on opposite sides of a prism-train, through which train the light is passed but once. The slit and observing eye-piece are thus far removed from each other, and the axes of the observing and collimating telescopes may be arranged to make any fixed angle with each other.

The general solution of the problem is effected by the introduction into some part of the spectroscopic train, between

\* "An Improved Form of Littrow Spectroscope," F. L. O. Wadsworth, *Phil. Mag.* July 1894.

† *Ibid.*

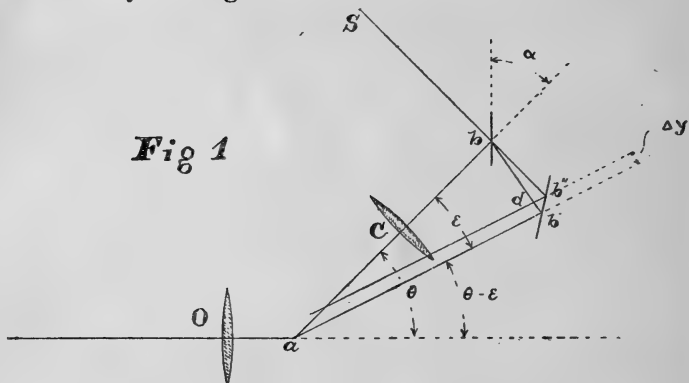
the slit and the focal plane of the observing lens, of a reflecting surface, which has an angular motion equal to one-half the change in angular motion of the ray refracted at minimum deviation. In the instruments of the Littrow type a reflector is also used, but for an essentially different purpose (to return the ray through the prism) and in an essentially different way from that here indicated. It hardly seems possible that the use of a reflecting surface in this way can be new, as it is something which would naturally suggest itself to anyone who might consider the problem; but no reference has been found to its employment, perhaps because the necessity for a "fixed-arm" spectroscope does not often seemingly arise. I hope to show, however, that at least some of the forms which have been developed during the last three years are simpler, more convenient, and less expensive than the ordinary form, and for spectrometric work quite as accurate. I will briefly describe these forms in the order of design and use, for this, perhaps, naturally is also the order of increasing simplicity.

*Case I.*—The case which first led me to a consideration of the problem was one in which it was desired to examine the radiations from a Geissler tube by means of the wave-comparer\*. Here the instrument which took the place of the usual observing eyepiece was a massive apparatus weighing about 500 pounds, which required great steadiness of mounting, while the Geissler tube, which itself served as the slit, was attached to a mercury-pump on one side and to a sodium-amalgam generating apparatus, with its attached drying-tubes, mercury-valves, &c., on the other, in such a way as to make its movement impossible. At first, indeed, the tube was mounted on a slit-arm of the spectroscope, sufficient flexibility being secured to allow of different lines being brought on the slit of the wave-comparer by the use of long lengths of glass tubing, but experiments soon showed that it was necessary to keep the passage from this Geissler tube to the pump as short and large as possible. If any considerable length of tubing intervened, unusual precautions had to be taken to keep all parts of it *perfectly* dry and clean, for only under these conditions, which, as the tubes were frequently changed, were almost impossible to maintain, could the McLeod gauge attached to the pump be relied upon to give, even approximately, the true pressure in the tubes, particularly when the electric discharge was passing.

The arrangement adopted in this case was that shown in plan

\* See a paper by Professor A. A. Michelson, "Application of Interference Methods to Spectroscopic Measurements," *Phil. Mag.* Sept. 1892.

in fig. 1, Pl. VIII. ; where  $t$  is the Geissler tube which serves as the source ;  $m$  a mirror, mounted on a vertical axis on the movable spectroscopic arm R ; and S the slit of the wave-comparer, which separates out the radiation which is to be analysed by the latter. To the lower end of the shaft which carries the mirror  $m$  is fixed a drum connected with a second drum  $a$ , fixed on the axis of the spectroscope by two steel cords. The drum  $a$  is just one half the size of  $b$ , and hence, as the arm R revolves about the axis of the spectroscope, the mirror  $m$  revolves on its own axis with an angular velocity just one half that of the arm, but in the opposite direction. Hence, if the mirror is once adjusted so that the direction of the reflected ray is parallel to the axis of collimation, it will remain parallel to that axis for all positions of the arm, and we have therefore a virtual rotation of the slit. There will be a slight lateral displacement of the ray, which can be easily investigated.



For a certain position of the arm, say  $a b$ , fig. 1, the reflected ray  $b a$  will lie in the principal axis of the collimating lens, which we will suppose passes through the centre of rotation of the mirror  $m$ . Let  $\theta$  be the angle of deviation for this position, then for any other position of the system in which the deviation is  $\theta \pm \epsilon$ , the reflected ray will be parallel to the axis of collimation, but will be displaced laterally from it a distance  $\Delta y$ . Finally, let  $\alpha$  be the angle between the mirror-face and the axis of collimation in the position  $a b$ , then, from the construction of the apparatus, this angle for any position  $b' a$  will be  $\alpha \mp \epsilon/2$ . From the two small triangles  $b' b'' d$  and  $b b' b''$  we get at once

$$\Delta y = b' b'' \cos (\alpha - \epsilon/2) = 2r \sin \frac{\epsilon}{2} \cos (\frac{\epsilon}{2} + 2\alpha),$$



where  $r$  is the distance between the spectroscope axis and the mirror axis. If  $\epsilon$  be small this expression is a minimum for  $\alpha=45^\circ$ , when the angle between the incident and reflected rays on  $m$  is a right angle. Under the conditions

$$\Delta y = -2r \sin^2 \frac{\epsilon}{2},$$

the angular error in the reading will evidently be

$$\delta = \frac{\Delta y}{R} = -\frac{2r}{R} \sin^2 \frac{\epsilon}{2}, \quad . \quad . \quad . \quad . \quad (1)$$

where  $R$  is the focal length of the collimator. For most prisms  $\epsilon$  will not exceed  $6^\circ$  from end to end of the spectrum, and hence, if we suppose  $\alpha=45^\circ$ , for the position of mean deviation we have for the maximum error  $\delta = .0013r/R$ , or if  $r/R = \frac{1}{10}$ ,  $\delta = 25''$ .

It is evident that there will be a change in the focal distance  $S, b, C$  as the arm revolves, which, under the conditions just assumed, would amount to about  $\frac{1}{200} R$ . This was not altogether a disadvantage, for when the lenses  $O$  and  $C$  are either or both of them simple lenses, we can, by choosing a value of  $r/R$  suitable to the particular prism used, very nearly compensate for the optical change in focus in passing from the violet to the red, or *vice versa*, by the mechanical lengthening or shortening of the path  $SbC$ . From an inspection of (1) it will be seen that the correction will diminish as the ratio  $r/R$  diminishes, and will become 0 for  $r=0$ , or for  $R=\infty$ . This indicated at once two methods of eliminating the error. The first and simplest is to place the mirror between the prism and collimator instead of between tube and collimator, as indicated in dotted lines in fig. 1 (Pl. VIII.). The second is to make  $r=0$  by placing the mirror-face in the axis of rotation of the spectroscope. To do this we must either place the prism considerably out of centre, fig. 2 (Pl. VIII.), or else we must place the mirror above or below the plane of refraction (fig. 3, Pl. VIII.). In either case a second reflector must be used to receive the beam from the first reflector  $m$  and return it to the prism. This second reflector may conveniently be a concave mirror of a focal length  $sm+mc$ , which will at the same time serve as collimator, or as objective of the observing-telescope. As the motion of the mirror is in this case the same in direction as that which must be imparted to the prism in order to keep it in minimum deviation, the mirror may be attached directly to the prism-table or to the prism itself\*. Which of these

\* The back of the prism may be polished and silvered, and arranged to act as the first reflector, as in fig. 2 *b*, Pl. VIII.

two latter forms is to be used will be determined by the conditions of use. The second form was the one employed when the wave-comparer was used in connexion with a spectrometer in experiments on wave-length measurements in the infra-red solar spectrum. In this form the ray is reflected out of the plane of incidence and refraction, and the spectrum is consequently inclined at a small angle to the horizontal, but in this case this was of no disadvantage as it involved only a slight rotation of the observing-slit in order to bring it parallel to the spectral lines.

*Case II.*—In the forms so far considered, no special conditions were imposed other than the general conditions of a fixed slit and a fixed observing instrument, it being possible to move the latter to meet the requirements of the particular optical systems which have been described. But in the next application of this system to the great spectrometer of the Astro-physical Observatory, an instrument in which the collimator has a focal length of nearly thirty feet, and the observing telescope a focal length of nearly twelve feet, another condition was imposed, viz. that the observing instrument (in this case the bolometer) should be in the prolongation of the axis of collimation. It was therefore necessary to avoid the lifting of the spectrum above the plane of incidence and refraction, and to place the mirror *m* at one side of the prism at such an angle to the latter that the direction of the reflected ray was parallel to the line of collimation as required. This throws the mirror-face out of the axis of rotation, and there is therefore a lateral displacement of the

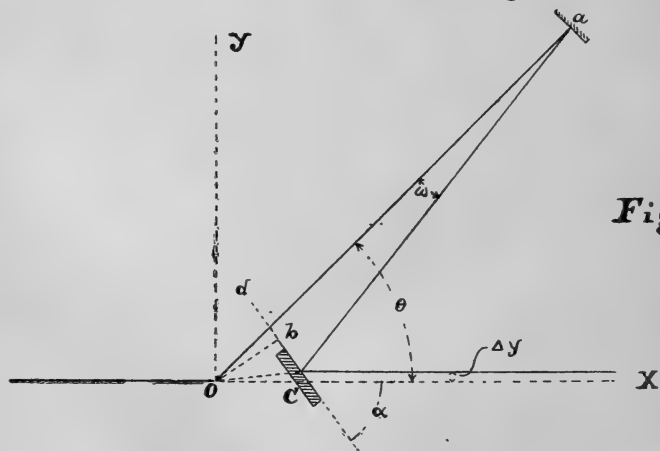


Fig 2

ray as the system rotates. A plan view of this arrangement is shown in fig. 2. It will be seen that the arrangement of

parts is essentially that employed in the first case described, except that a concave mirror is now used instead of the lens. The calculation of the lateral displacement, although not quite so simple as in the first case, is easy.

In fig. 2,

let  $d$  = distance  $oa$  from axis of rotation to the face of the concave mirror ;

$r$  = perpendicular distance  $ob$  from the axis to the plane of the reflecting-mirror ;

$\omega$  = angle  $oac$  ;

$\theta$  and  $\alpha$  have the same meanings as before.

When in adjustment the line of collimation passes through the axis of the rotation, and the deflected ray  $oa$  will fall on the centre of the concave mirror. Then we have from analytical geometry the following equations:—

For the line  $ac$ ,

$$y = \tan (\theta + \omega) [\chi - d \cos \theta] + d \sin \theta \\ = - \tan 2\alpha [\chi - d \cos \theta] + d \sin \theta, \quad . \quad . \quad . \quad (2)$$

since  $\theta + \omega = 180^\circ - 2\alpha$ ;

and for the line  $dc$ ,

$$y = - \tan \alpha (\chi) + \frac{r}{\cos \alpha} \quad . \quad . \quad . \quad . \quad (3)$$

The lateral displacement ( $\Delta y$ ) of the ray will be the ordinate of the point of intersection of these two lines. Solving (2) and (3) for  $y$  we have

$$\Delta y = d \sin (2\alpha + \theta) - 2r \cos \alpha.$$

If the system be turned through a small angle  $\epsilon$ ,  $\theta$  becomes  $\theta + \epsilon$ , and  $\alpha$  becomes  $\alpha - \epsilon/2$ . Hence  $\theta + 2\alpha = \text{const.}$ , and

$$\Delta y' = d \sin (\theta + 2\alpha) - 2r \cos (\alpha - \epsilon/2),$$

$$\Delta y - \Delta y' = 2r [\cos \alpha - \cos (\alpha - \epsilon/2)] \cong r \cos (\theta + \omega) \sin \epsilon;$$

or the lateral displacement is directly proportional to  $r$ , to the cosine of the angle of deviation, and to the angle of displacement. Since  $\epsilon$  is fixed by the prism used, and  $\omega$  must be small in order to secure good definition, the only way in which the error of displacement may be reduced is by reducing  $r$ ; hence the object in placing the mirror just as close to the prism as possible. In the actual case, the values of  $r$ ,  $\theta$ , and  $\omega$  were

$$r \cong 10 \text{ centim.}, \quad \theta \cong 50^\circ \text{ (for D lines)}, \quad \text{and } \omega \cong 3^\circ.$$

Hence for  $\epsilon = 3^\circ$  we have  $\Delta y' = 3$  millim., and the angular error is, as before,  $3/R = \frac{3}{3560} = 3'$  nearly.

It will readily be seen that if we do not impose the condition that the reflected ray shall be parallel to the line of collimation, we may place the mirror so that the displacement will be almost *nil* for even very considerable values of  $r$ . This general case may be readily worked out by introducing into the above another angle,  $\beta$ , which is the angle between the axis of collimation and the ray reflected from the mirror, connected with the angles  $\theta$  and  $\alpha$  by the relation

$$\theta + \omega = 180 - (2\alpha + \beta).$$

In this case it will be found, as might have been expected, that the displacement is a minimum when the angle  $\alpha$  is as nearly as possible equal to  $\theta$ , viz., when the angle of incidence on the mirror is as nearly as possible  $90^\circ$ . In the most unfavourable case, however, the correction, although considerable, is not of sufficient magnitude to become objectionable in spectroscopic work. In such work it is not even necessary to apply the correction, as the effect is the same as would be produced by a slight change in the optical properties of the prism. The displacement might in this, as in the former case, have been eliminated by making  $R = \infty$ , viz., by substituting for the concave mirror at  $a$  a plane reflector and placing the image-forming objective beyond the reflecting surface  $m$ ; but the additional reflecting surface was objectionable as diminishing the brightness of the spectrum.

*Case III.*—The arrangement last described was used with a considerable degree of success for some time, but when some very accurate angular measurements were attempted with it a difficulty of a mechanical character presented itself. It will be noted that the correct working of this—as of all systems so far described—depends on the maintenance of an exact ratio of 2 to 1 between the angular motions of the spectroscope-arm and of the reflecting mirror. It is necessary to maintain the prism at minimum deviation in all spectro-metric measurements; but not with any great degree of exactness, as an error of  $2'$  or  $3'$  in the angular position of the prism will not affect the deviation by more than  $\frac{1}{50}$  of this amount. But with the mirror any error in angular position with respect to the arm will change the angular direction of the refracted and reflected ray by double that amount; and hence if we wish to determine any angle of deviation to within  $10''$ , we must be sure of the position of the mirror to within less than  $5''$ . To secure this degree of accuracy mechanically and automatically with any ordinary minimum deviation attachment is out of the question, for an error of  $5''$  in angular position means in linear measurement an error of only  $\frac{1}{1000}$  millim. at the end of an arm

40 millim. long. Probably this degree of accuracy could be secured if necessary by the use of a minimum deviation attachment of pure linkwork, like that shown in fig. 4 (Pl. IX.), which is far superior in every respect to the ordinary sliding link-form usually placed on a spectroscope\*. It may also be secured by the system first described, because in it any required degree of accuracy may be reached by an increase in size of the drums *a*, *b*.

It was at first thought that a return to this system would be necessary; but while considering how this could best be done, the idea of another simple system, which did away with all mechanical arrangements, presented itself. It is derived from the first modification of the earlier system (fig. 1, Pl. VIII.) very easily by suppressing entirely the movable spectroscope-arm and securing the reflecting mirror rigidly to the prism. It will evidently have the same angular motion as before, and will therefore reflect a ray which passes through the prism at minimum deviation in the same direction for all positions of the latter, or *vice versa*. With this arrangement it is evident that there will be no error due to mechanical inaccuracies of the moving parts because there is no longer any relative motion between them, both prism and mirror being fixed relatively to each other. But it would appear at first sight that for large angles of deviation the light would fall upon a very different part of the reflecting mirror to that which it would for small angles, and that a large lateral displacement of the reflected ray might be expected in consequence. The lateral shifting is no great detriment if a collimator is used, and the beam which passes through the prism is a strictly parallel one, for then its effect is simply to necessitate the loss of some light, or else the use of larger lenses to provide for this shifting. But where only one objective is used, as in the simpler forms of instruments, or for some special reason in the better ones† (see fig. 7, Pl. IX.), and the beam through the prism is in consequence conical, the lateral displacement gives rise, as already explained, to an angular error depending on the radius of curvature of the wave-front of the incident beam. This error, or, more properly, correction, was especially objectionable in the particular work then in hand, in which it was very desirable to maintain an exact relationship between the angular reading of the spectrometer-circle (in which prism and mirror were mounted), and the wave-length of the radiation falling on what corresponded

\* Kempe, 'Lecture on Linkages,' p. 40.

† In this case it was desirable in order that there might be as little loss by reflexion and absorption as possible.

to the cross-wire of the observing telescope. On examination of the geometrical path of the ray through the system just indicated, it was unexpectedly found that if two simple conditions were fulfilled, the refracted ray was, after reflexion, not only constant in direction but also constant in position, viz., that there was no lateral displacement for different wavelengths, and consequently no angular correction required for either plane or spherical waves. To find these necessary conditions, let us first consider the general case in which the axis of rotation and the reflecting-mirror are in any position with reference to the line of collimation.

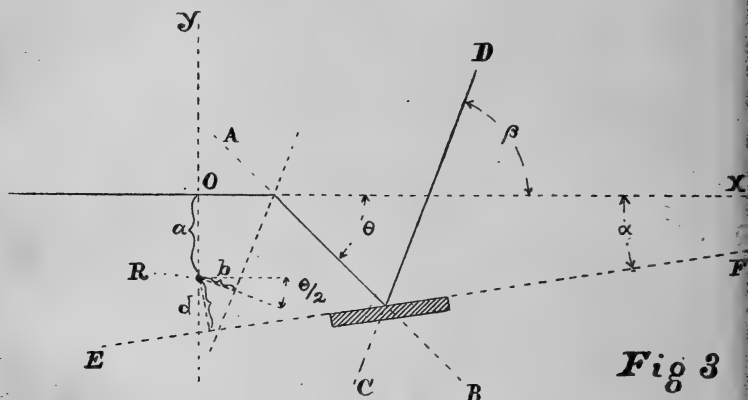


Fig 3

Let the axis of collimation be the X axis, and let a line passing through the axis of rotation R be the Y axis. Let  $d$  be the perpendicular distance from the axis of rotation to the plane of the mirror-face; let  $b$  be the perpendicular distance from the same point to the plane bisecting the angle of the prism (and hence bisecting also the angle of deviation of the ray at minimum deviation), and let  $a$  be the  $y$  coordinate of this point. Then the equation of the line EF (the intersection of the plane of the reflecting surface with the XY plane) will be

$$y = \tan \alpha x - \frac{d + a \cos \alpha}{\cos \alpha};$$

and of the line AB (refracted ray),

$$y = -\tan \theta x + \frac{2 \sin \theta/2}{\cos \theta} \{ \sin \theta/2 + b \}.$$

The coordinates of the points of intersection of these two lines will therefore be

$$\begin{aligned}
 x' &= \frac{\frac{2 \sin \theta/2}{\cos \theta} [a \sin \theta/2 + b] - \frac{d + a \cos \alpha}{\cos \alpha}}{\tan \alpha + \tan \theta}, \\
 &= \frac{2 \sin \theta/2 \cos \alpha [a \sin \theta/2 + b] - (d + a \cos \alpha) \cos \theta}{\sin (\alpha + \theta)}, \\
 y' &= \frac{2 \sin \theta/2 [a \sin \theta/2 + b] \tan \alpha - \frac{d + a \cos \alpha}{\cos \alpha} \tan \theta}{\tan \alpha + \tan \theta} \\
 &= \frac{2 \sin \theta/2 \sin \alpha [a \sin \theta/2 + b] - (d + a \cos \alpha) \sin \theta}{\sin (\alpha + \theta)}.
 \end{aligned}$$

The equation of the reflected ray CD will be

$$y - y' = \tan (\theta + 2\alpha) (x - x'),$$

and the length of the perpendicular let fall from the origin will be

$$p = \frac{\tan (\theta + 2\alpha) x' - y'}{\sqrt{1 + \tan^2 (\theta + 2\alpha)}} = x' \sin (\theta + 2\alpha) - y' \cos (\theta + 2\alpha),$$

Substituting the values of  $x'$  and  $y'$ , reducing, and introducing the relations

$$\theta + 2\alpha = \beta = \text{constant},$$

$$\theta + \alpha = (\beta - \alpha),$$

we finally obtain

$$p = 2a \cos^2 \beta/2 + 2b \sin \theta/2 + 2d \cos (\alpha + \theta).$$

The term  $2a \cos^2 \beta/2$  is a constant, but the last two terms are variable. It will be seen at once that we may make  $p$  a constant, viz., prevent any lateral shifting of the ray, by simply making both  $b$  and  $d$  equal to zero. In other words, if we simply fulfil the condition that the axis of rotation of the system shall be at the intersection of the plane bisecting the refracting angle of the prism with the plane of the reflecting mirror, there will be no lateral displacement of the ray which passes through the system at minimum deviation, for different values of  $\theta$ , viz. for different wave-lengths. There is one case in which this does not hold, viz., when these two planes are parallel. Then we have

$$\alpha = 90^\circ - \theta/2, \text{ or } \alpha + \theta = 180^\circ - \alpha.$$

Hence

$$b \sin \theta/2 + d \cos (\alpha + \theta) = (b - d) \cos \alpha;$$

and therefore we may in this case make  $p$  constant by making  $b = d$ : in other words, by making the two planes coincident. Then the second half of the prism becomes useless, and we

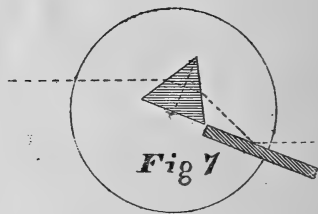
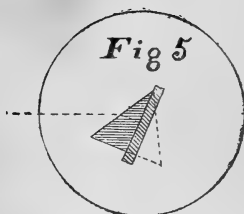
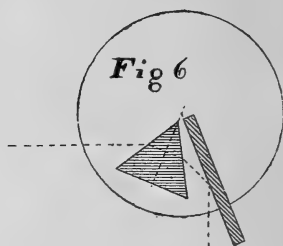
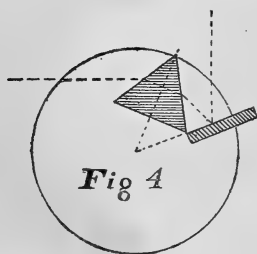
have the original half-prism form of Littrow, fig. 5, which is now seen to be only one special form of a general class. It is evident that by varying the angle  $\alpha$  we may make the angle  $\beta$  anything we please from 0 to  $360^\circ$ . Four special cases only are considered :—

(1) When  $\beta = 90^\circ$ , then for  $\theta = 45^\circ$  we have  $\alpha = 22\frac{1}{2}^\circ$ . The arrangement of the parts is shown in fig. 4.

(2) When  $\beta = 180^\circ$ ,  $\alpha = \frac{1}{2}\theta$ , and we have the Littrow half-prism arrangement already referred to (fig. 5).

(3) When  $\beta = 270^\circ$ , for  $\theta = 45^\circ$ ,  $\alpha = 112\frac{1}{2}^\circ$ , and we have the arrangement shown in fig. 6.

(4) Finally, when  $\beta = 0$  the reflected ray is parallel to the coincident, and now  $\alpha = -\theta/2$  (fig. 7).



In all these last forms the prism-mirror system is mounted directly on the graduated circle of the spectrometer and revolves with it. Since the angular rotation of the prism is exactly one half that of the refracted ray which passes through it at minimum deviation, it follows that we may determine angular deviations from the readings of the spectrometer circle, just as in the ordinary forms of the instrument, except that the angular readings must be multiplied by 2 to obtain the angular deviations. The movable parts of the instrument (the mirror and prism) are therefore rendered extremely light and mobile, without any sacrifice in accuracy,



while incidentally the more or less troublesome minimum-deviation attachment is done away with. The last arrangement, which is in one sense a direct-vision spectroscope with but a single prism, fulfils the condition of parallelism between the refracted reflected ray and the incident ray, and it is therefore the one which has been finally adopted for the spectro-bolometer of the Observatory in place of the form first used on that instrument\*.

A plan view of the mounting in this particular form of instrument is shown in fig. 5, Pl. IX., and a side view (photograph) in Pl. X. It will be seen that the prism and mirror are mounted together in a single frame AA, provided with three levelling-screws which rest, one in a conical hole, the second in a slot, and the third on a plane; so that the whole frame may readily be removed from the spectrometer table and then replaced in exactly the same position. The triangular prism-table B is arranged to slide vertically in the guides *a b*, and thus provide for prisms of different heights. The table has a motion of adjustment regulated by the screw *c*, about a line parallel to the mirror-face, for the purpose of bringing the refracting edge of the prism parallel to that face, and is provided with screws *e, f, g, h*, which serve to adjust the prism laterally and in angle, so that in the first place the plane bisecting the refracting angle may pass through the axis of rotation, and, secondly, so that the prism-faces may make equal angles with the faces of the mirror (the minimum-deviation condition). It will be observed that when these screws are once adjusted they serve as stops which will bring any prism (of standard  $60^\circ$  angle) that may be used into the correct position; for, if smaller than the prism for which they

\* Since writing the above my attention has been called to an article in *Zeit. für Instrumentenkunde* for November 1881, describing this particular "direct-vision" arrangement of the prism and mirror. There was, however, no indication of the general class of which this is but a particular type, and hence, of course, no indication of the conditions which it was necessary to fulfil to prevent a lateral shifting of the beam; indeed, the author seems to accept this lateral shifting as a necessary condition, for he says "Der im Minimum der Ablenkung durchgehende Strahl wird also bei dieser Anordnung nur seitlich etwas verschoben."

Professor Langley had also quite independently used this particular arrangement of prism and reflecting mirror in a modification of Foucault's "Lifting Prism" for separating different orders of superposed grating-spectra. In his use of it the lateral displacement was recognized as objectionable, and was mechanically corrected for by an ingenious arrangement, designed by Mr. C. T. Child, then assistant in the Observatory, which imparted to the mirror a small angular motion, just sufficient to correct for the angular displacement of the spectral image, as the whole system travelled down through the spectrum.

were adjusted, it is only necessary either to turn each one in a measured amount, or, more simply, insert a thin piece of glass or metal between the screws on each side and the prism. A still better plan, if many prisms are to be used, is to have each prism mounted on a base of the required size on which it has been adjusted once for all and then cemented. The adjustment, as will be shown hereafter, does not need to be particularly accurate.

The mirror and prism having been adjusted to each other and to the spectrometer axis once for all, the other adjustments preliminary to the use of the instrument are very simple. The first operation is to make the axes of the collimating and observing telescopes parallel. This is most simply done by removing the prism-mirror system and allowing the beam for the collimator to fall directly on the objective of the view-telescope. Since the constant lateral displacement of the beam by the system will be  $2a$ , it follows that if the aperture of the telescope is, say,  $2\frac{1}{2}a$ , sufficient light will fall upon the second objective to form a distinct image of the slit. Since, however, the use of such a small portion of the objective is apt to cause a lateral shifting of the image, it is better either to mount the view-telescope on a short cross slide, or on a rocking arm, the motion of which is accurately rectilinear, or, what is better, to use a small double-reflection prism, fig. 6 *b* (Pl. IX.), which will laterally deflect the beam by the amount required. If a system like that in fig. 7 (Pl. IX.) is used, the simplest method of initially setting the direct image on the cross wire of the observing telescope is to set up at the side of the slit and at an accurately measured distance  $2a$  from its centre, a second slit or fine point, and bring the image of this to the centre of the field.

The second step is to determine the zero of graduation, which is done by replacing the optical system and revolving the mirror until it is perpendicular to the line of collimation. With the first form of instrument this is accomplished simply by bringing the image of the slit into coincidence with the slit itself; in the second form it is most conveniently done by setting up a point at a distance from the mirror equal to the principal focal distance, bringing this point into the line *bms* by removing the eyepiece and sighting with the eye past the cross wire at the distant point *s*, and then revolving the mirror until the image of this illuminated point coincides with the point itself. The reading of the circle corresponding to this position of the mirror is called the zero reading. The prism is then replaced in position by being brought against the screws *e*, *f*, *g*, *h*, and the whole system revolved

until the desired part of the spectral field is brought into the observing eyepiece. If the spectrum is now either too high or too low, it shows that the refracting edge of the prism is slightly inclined to the mirror-face, and the screw *c* is turned until the spectrum is centred. Then, if all the preliminary adjustments have been properly made, the angular deviation of the central ray in the field will be given by the relation

$$\theta = 2(\beta - (90^\circ + \alpha)),$$

where  $\beta$  is the circle-reading for a deviation  $\theta$ , and  $\alpha$  is the zero-reading determined as already described.

In very accurate spectrometric work it is important to determine just what degree of accuracy is required in making the various adjustments of parts to each other in order to attain a given degree of accuracy in the final result. The theory of these adjustments is comparatively simple, but somewhat lengthy, and it will therefore be briefly indicated in a future paper.

Astro-Physical Observatory,  
Washington, D.C, March 1893.

### XXXIX. *On the Highest Wave of Permanent Type.*

By J. McCOWAN, M.A., D.Sc., *University College, Dundee\**.

IN a previous communication†, in which I discussed the general theory of the class of waves in water or other liquid which have no finite wave-length but which are of permanent type, that is to say, which are propagated with constant velocity without change of any kind, I gave a rough estimate of the maximum height to which such waves might attain without breaking. The paper dealt chiefly with an approximation which was specially suitable for waves of small or moderate elevation, and it is the object of the present paper, therefore, to supplement this by investigating an approximation better adapted to the discussion of the extreme case of the wave at the breaking height, and sufficiently exact for ordinary purposes. I trust, however, to be soon able to communicate a fuller discussion of the general theory of the solitary wave which I have almost completed.

#### 1. *The General Equation of the Motion.*

The highest wave which can be propagated without change in water of any given depth is obviously the highest solitary

\* Communicated by the Author, having been read before the Edinburgh Mathematical Society, June 8, 1894.

† "On the Solitary Wave," *Phil. Mag.* July 1891.



satisfied for a solitary wave, with the exception of the condition of constant surface-pressure, are identically satisfied by (1): for  $w$  vanishes with  $z$ , and when  $x = \pm \infty$ ,  $u = -U$  and  $w = 0$ . We proceed, therefore, to determine the surface-pressure with a view to the determination of the available constants so as to satisfy as nearly as may be this condition for a *free* surface: as it is, (1) may be regarded as giving a particular *forced* wave.

## 2. The Surface-Pressure near the Mean Level.

Expanding (1), and writing for brevity

$$\alpha = 1 + 2f, \quad \beta = 1 - 4f, \text{ \&c., } \dots \dots (3)$$

we get

$$-(u + iw)/U = 1 - \frac{1}{2}\alpha k^2 \sec^2 \frac{1}{2}m(z + ix) - \frac{1}{8}\beta k^4 \sec^4 \frac{1}{2}m(z + ix); \quad (4)$$

therefore, further, for  $x$  positive

$$-(u + iw)/U = 1 - 2\alpha k^2 e^{-m(x-iz)} + 2(2\alpha - \beta k^2)k^2 e^{-2m(x-iz)} \text{ \&c.; } \quad (5)$$

therefore, integrating with respect to  $z + ix$ ,

$$-m(\psi + i\phi)/U = m(z + ix) + 2i\alpha k^2 e^{-m(x-iz)} - i(2\alpha - \beta k^2)k^2 e^{-2m(x-iz)}. \quad (6)$$

Now if  $h$  be the mean depth, or the depth at an infinite distance from the crest, we must, taking  $\psi = 0$  at the bottom, have  $\psi = -Uh$  at the surface. Also, if  $\eta$  denote the elevation of the surface at any point above the mean level, we must have  $z = h + \eta$  at the surface. Substituting these values in the expression for  $\psi$  involved in (6), we obtain as the equation to the surface,

$$m\eta = 2\alpha k^2 e^{-m\eta} \sin m(h + \eta) - (2\alpha - \beta k^2)k^2 e^{-2m\eta} \sin 2m(h + \eta) \dots;$$

or, when  $\eta$  is small,

$$m\eta = 2\alpha k^2 e^{-m\eta} \sin mh - (2\alpha - \beta k^2 - 2\alpha^2 k^2)k^2 e^{-2m\eta} \sin 2mh \dots; \quad (7)$$

which gives the equation to the surface in a convenient form for points not too near the crest.

Again, from (5) we get

$$q^2/U^2 = 1 - 4\alpha k^2 e^{-m\eta} \cos mz + 4k^2 e^{-2m\eta} \{ (2\alpha - \beta k^2) \cos 2mz + 4\alpha^2 k^2 \}; \quad (8)$$

therefore, by (7), we have at the surface where  $\eta$  is small,

$$q^2/U^2 = 1 - 4\alpha k^2 e^{-m\eta} \cos mh + 4k^2 e^{-2m\eta} \{ (2\alpha - \beta k^2) \cos 2mh + \alpha^2 k^2 (1 + 2 \sin^2 mh) \} \dots \quad (9)$$

Now in a liquid of density  $\rho$  moving irrotationally acted on by no force but gravity, the pressure  $p$  at any point is given by

$$p = \text{constant} - \frac{1}{2}\rho q^2 - g\rho z; \quad \dots \dots (10)$$

and therefore if  $\delta p$  denote the excess of pressure at any point on the surface over that at the mean level, we have

$$\delta p = \frac{1}{2} \rho (U^2 - q^2) - g p \eta; \quad . \quad . \quad . \quad (11)$$

whence, on substituting for  $\eta$  and  $q^2$  from (7) and (9), we get

$$\delta p / \rho U^2 = 2 \alpha k^2 \epsilon^{-m x} \{ \cos m h - g/m U^2 \cdot \sin m h \} + \&c. \quad (12)$$

Now for a free surface  $\delta p$  ought to vanish; therefore for a first approximation we must take

$$\cos m h - g/m U^2 \cdot \sin m h = 0;$$

that is,

$$U^2 = g/m \tan m h; \quad . \quad . \quad . \quad (13)$$

and (12) becomes, writing it out to the next term,

$$\delta p / \rho U^2 = 2 k^2 \epsilon^{-2 m x} \{ (2 \alpha - \beta k^2) \sin^2 m h - 3 \alpha^2 k^2 \}. \quad . \quad . \quad (14)$$

The coefficient of  $\epsilon^{-2 m x}$  in (14) ought of course to be made to vanish; but it will be preferable for our present purpose to retain it as a small pressure-error, and so leave another of our constants available to satisfy the conditions in the neighbourhood of the crest to which we proceed.

### 3. *The Surface-Pressure near the Crest.*

Put  $z = c - \zeta$ , so that  $\zeta$  vanishes at the crest; then, writing for brevity

$$\left. \begin{aligned} p &= \tan \frac{1}{2} m c, \\ A &= 1 - f, \\ B &= \{ (1 + 11 p^2) f - (1 + 3 p^2) \} / 8 p, \end{aligned} \right\} \quad . \quad . \quad (15)$$

we get, on expanding (1) in powers of  $\zeta - ix$ ,

$$-(u + iv)/U = \sqrt{pm(\zeta - ix)} \{ A + Bm(\zeta - ix) + \&c. \}; \quad (16)$$

whence, integrating with respect to  $\zeta - ix$ , we get

$$m(\psi + i\phi)/U - m\psi_0/U = 2\sqrt{p} \{ m(\zeta - ix) \}^{\frac{3}{2}} \{ \frac{1}{3} A + \frac{1}{5} Bm(\zeta - ix) \}.$$

where  $\psi_0$  is the value of  $\psi$  at the crest.

Put

$$\zeta = r \cos \vartheta, \quad x = r \sin \vartheta, \quad . \quad . \quad . \quad (18)$$

then (18) gives for the surface, determined by  $\psi = \psi_0$ ,

$$\frac{1}{3} A \cos \frac{3}{2} \vartheta + \frac{1}{5} B m r \cos \frac{5}{2} \vartheta + \&c. = 0. \quad . \quad . \quad (19)$$

Thus when  $r=0$ ,  $\vartheta = \pm \frac{\pi}{3}$ , showing that the crest is formed by two branches equally inclined to the bottom cutting at an angle of  $120^\circ$ .

Put then

$$\vartheta = \frac{\pi}{3} + \sigma;$$

∴ (19) gives when  $\sigma$  is small,

$$\sigma = -Bmr/5A, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

as a convenient approximation for the form of the surface in the neighbourhood of the crest.

Again, (11) may be written

$$\delta p = \frac{1}{2}\rho(U^2 - q^2) - gp(c - h - \zeta), \quad . \quad . \quad . \quad . \quad (21)$$

whence, since  $q$  and  $\zeta$  vanish together, to make  $\delta p$  vanish we must have

$$U^2 = 2g(c - h), \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and this reduces (21) to

$$\delta p = gp\zeta - \frac{1}{2}\rho q^2. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Now from (16) we obtain

$$q^2/U^2 p m r \{A^2 + 2ABm\zeta + \&c.\}, \quad . \quad . \quad . \quad (24)$$

and thus

$$\delta p = \rho r \{g \cos \vartheta - \frac{1}{2}mA^2pU^2 + ABU^2m\zeta + \&c.\}. \quad . \quad (25)$$

Hence, since  $\vartheta = \frac{\pi}{3} + \sigma$  we must have, to make  $\delta p$  vanish to a first approximation,

$$g \cos \frac{\pi}{3} - \frac{1}{2}mA^2pU^2 = 0,$$

that is

$$U^2 = g/mA^2p, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

and (25) becomes

$$\delta p/\rho U^2 = -\frac{1}{2}\left(1 - \frac{\sqrt{3}}{5}\right)pABm^2r^2 + \&c. \quad . \quad . \quad (27)$$

This cannot vanish unless  $B$  vanishes, in which case we see by (20) that the curvature of the surface vanishes close to the crest. This result is obviously independent of our approximation, but we have not taken enough of constants to secure it here: it will be found, however (v. § 5), that the other equations determining the constants we have at our disposal will make  $B$  very approximately vanish.

#### 4. Numerical Determination of the Constants.

There is still one important condition to be satisfied. To ensure the connexion between our separate treatment of the neighbourhoods of the crest and mean level, we must secure that the stream-line  $\psi = -Uh$ , bounding the distant surface, shall pass through the crest: or, in other words, the flow across any infinitely distant section must be equal to the flow

across the axis of  $z$ . This condition may be written, by (1)

$$h = \int_0^c (1 - f k^2 \sec^2 \frac{1}{2} m z) \sqrt{1 - k^2 \sec^2 \frac{1}{2} m z} . dz, \quad (28)$$

which gives, remembering that  $k = \cos \frac{1}{2} m c$ ,

$$m h = \pi \{ 1 - \cos \frac{1}{2} m c - \frac{1}{4} f \sin \frac{1}{2} m c . \sin m c \}. \quad (29)$$

We may now proceed to evaluate the constants in (1) in terms of  $h$  the mean depth of the liquid in the channel.

Eliminating  $U^2$  between (22) and (13) we get

$$m c = m h + \frac{1}{2} \tan m h, \quad . \quad . \quad . \quad (30)$$

while (13) and (26) give

$$(1 - f)^2 = \cot m h \cot \frac{1}{2} m c. \quad . \quad . \quad . \quad (31)$$

If now we solve equations (29), (30), and (31) for  $m, c$ , and  $f$ , we shall find  $m h = 1.0025$  approximately: hence, remembering that at best the surface-pressure is only to be approximately constant, it will be sufficient to take for our present purpose

$$m h = 1, \quad . \quad . \quad . \quad (32)$$

and it is just possible that this may be the exact value.

Substituting this value in (30) we get

$$c \doteq 1.78 h. \quad . \quad . \quad . \quad (33)$$

This gives for the maximum wave-height

$$c - h = \eta_0 = .78 h, \quad . \quad . \quad . \quad (34)$$

which differs by less than the experimental error from the value  $.75 h$  which I have already {S. § 10} given as a fair average of some experiments I made in connexion with my former paper.

Again, from (13) and (32), or (22) and (34), we obtain for the velocity

$$U^2 \doteq 1.56 g h, \quad . \quad . \quad . \quad (35)$$

which shows that the maximum wave travels about 25 per cent. faster than low waves in the same depth of channel.

Finally, substituting from (32) and (33) in (31) we get

$$f \doteq .28. \quad . \quad . \quad . \quad (36)$$

We have now only to substitute the values of the constants just determined in our general equations.



5. *The Final Equations of the Motion.*

The fundamental equation (1) may now be written

$$u + w = -1.25 \sqrt{gh} \{1 - .11 \sec^2 \frac{1}{2}(z + \iota x)/h\} \sqrt{1 - .40 \sec^2 \frac{1}{2}(z + \iota x)/h}, \quad (37)$$

which completely determines the motion of the fluid.

It is convenient, however, to consider the formulæ specially suitable to the regions near to, and fairly distant from, the crest. Thus for regions fairly distant from the crest (where  $\exp(-x/h)$  is small) (5) and (6) give

$$-(u + w)/U \doteq 1 - 1.24 \epsilon^{-(x - \iota x)/h} + \&c., \quad (38)$$

and

$$-(\psi + \iota \phi)/Uh = (z + \iota x)/h + \iota 1.24 \epsilon^{-(x - \iota x)/h} - \&c., \quad (39)$$

in which  $U$  has the value given by (35).

The equation to the free surface, as given by (7), becomes

$$\eta/h = 1.04 \epsilon^{-x/h} - .44 \epsilon^{-2x/h} \&c., \quad (40)$$

and for the pressure-error given by (14) we have

$$\delta p \doteq - .89 \epsilon^{-2x/h} gph. \quad (41)$$

Again, for the neighbourhood of the crest (16) and (17) give

$$-(u + w)/U \doteq .80 \sqrt{(\zeta - \iota x)/h} \{1 + .084(\zeta - \iota x)/h\}. \quad (42)$$

and

$$(\psi + \iota \phi)/Uh = 1 + .53 \{(\zeta - \iota x)/h\}^{3/2} \{1 + .50(\zeta - \iota x)/h\}. \quad (43)$$

We have already seen that the crest is formed by two surfaces, equally inclined to the bottom, meeting at an angle of  $120^\circ$ , so that the summit of the wave has the form of a blunt wedge. We have also seen that in the free wave these surfaces must be plane or have an infinite radius of curvature at the crest; we have, however, made no effort to satisfy this condition, but on substituting the values of the constants in (20) we find that it gives the radius of curvature at the crest about equal to thirty times the depth of the water, a result sufficiently indicating the closeness of our approximation.

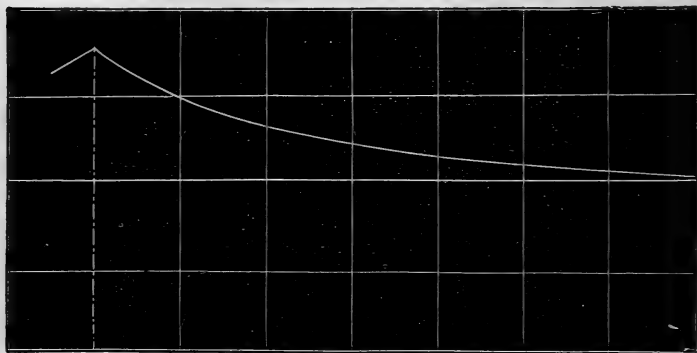
The pressure-error near the crest, as given by (27), is

$$\delta p \doteq .03 gpr^2/h. \quad (44)$$

By (41) and (44) we see that the deviation from constant surface-pressure is everywhere very small; there is a very slight excess near the crest but vanishing at the crest, and a slight defect near the mean level. The deviation has in fact only an appreciable value over a very limited region, say from  $x = .5h$  to  $x = 1.5h$ ; (41) and (44) are hardly applicable

within this region, but I estimate that within it the maximum defect of pressure is less than that of a head of water, or whatever other liquid the channel may contain, of one tenth of the mean depth.

The accompanying figure shows the form of the wave, only half of it being drawn, however, as the wave is symmetrical



about the crest. The thicker straight line indicates the bottom of the channel, while the mean depth is shown by a finer line to which the surface approaches asymptotically.

***XI. On the Velocity of the Cathode-Rays. By J. J. THOMSON, M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge\*.***

**T**HE phosphorescence shown by the glass of a discharge-tube in the neighbourhood of the cathode has been ascribed by Crookes to the impact against the sides of the tube of charged molecules driven off from the negative electrode. The remarkably interesting experiments of Hertz and Lenard show that thin films of metal when interposed between the cathode and the walls of the discharge-tube do not entirely stop the phosphorescence. This has led some physicists to doubt whether Crookes's explanation is the true one, and to support the view that the phosphorescence is due to ætherial waves of very small wave-length, these waves being so strongly absorbed by all substances that it is only when the film of the substance is extremely thin that any perceptible phosphorescence occurs behind it. Thus on this view the phosphorescence is due to the action of a kind of

\* Communicated by the Author.

ultra-violet light, which possesses in an exaggerated degree the property possessed by the ultra-violet rays of the sun of producing phosphorescence when incident upon such substances as German or uranium glass. It is perhaps worth while to observe, in passing, that the light produced in an ordinary discharge-tube by an intense discharge is very rich in phosphorogenic rays. I have been able to detect phosphorescence in pieces of ordinary German-glass tubing held at a distance of some feet from the discharge-tube, though in this case the light had to pass through the glass walls of the vacuum-tube and a considerable thickness of air before falling on the phosphorescent body.

The view, to which Lenard has been led by his experiments, that the cathode-rays are ætherial waves demands the most careful consideration and attention; for if it is admitted, it follows that the æther must have a structure either in time or space. For these cathode-rays are deflected by a magnet, which, so far as our knowledge extends, does not produce any effect on ultra-violet light unless this is passing through a refracting substance: thus if the cathode-rays are supposed to be ultra-violet light of excessively small wave-length, it follows that in the æther in a magnetic field there must either be some length with which the wave-length of the cathode-rays is comparable, or else some time comparable with the period of vibration of these rays.

It might be objected that it is possible that the action of a magnet on the cathode-rays is a secondary effect, and that the primary action of the magnet is to affect the main current of the discharge passing between the positive and negative electrodes, and thus to alter the distribution of the discharge entering the cathode: this would affect the distribution of the places of greatest intensity over the cathode, and thus indirectly the distribution of the waves emerging from it. To test this point I shielded the cathode from magnetic forces by means of a magnetic screen consisting of a ring made of soft iron wire: the length was about 1.5 inch, its thickness was about .75 inch. When this ring encircled the cathode a magnet was brought up to the tube: the phosphorescent patches inside the ring were not now affected by the magnet, but those on the parts of the tube farther away from the cathode and outside the iron ring were very much displaced by the magnet; thus proving that the magnet acts on the cathode-rays through the whole of their course, and does not merely affect the place on the cathode at which they have their origin. There thus seems no escape from the conclusion that the establishment of the hypothesis that the cathode-rays

are ætherial rays would also prove the finiteness of the structure of the æther.

The following experiments were made with the view of determining the velocity with which the cathode-rays travel, as it seemed that a knowledge of this velocity would enable us to discriminate between the two views held as to the nature of the cathode-rays. If we take the view that the cathode-rays are ætherial waves, we should expect them to travel with a velocity comparable with that of light; while if the rays consist of molecular streams, the velocity of these rays will be the velocity of the molecules, which we should expect to be very much smaller than that of light.

The method I employed is as follows:—The discharge-tube was sealed on to the pump, and the two electrodes were placed at the neck of this tube. The discharge-tube was covered with lampblack, with the exception of two thin strips in the same straight line from which the lampblack was scratched: these strips were about 10 centim. apart; the one nearest to the negative electrode was about 15 centim. from the electrode, the other was 25 centim. from the electrode. They were chosen so as to phosphoresce with, as nearly as could be judged, equal brilliancy when the discharge passed through the tube.

The light from the phosphorescent strip fell upon a rotating mirror about 75 centim. from the tube. This mirror is the one used by me in my experiments on "The Velocity of Propagation of the Electric Discharge through Gases" (Proc. Roy. Soc. 1890), and is described in that paper. The only change made in the mirror was to replace the single plane strip of silvered glass which was used in the previous experiments by six strips of mirror fastened symmetrically round the axis. The mirror was driven by a large gramme-machine.

The images formed by reflexion from the mirror were observed through a telescope, of which the object-glass was a large portrait photographic lens of 4-inch aperture, the eyepiece a short-focus lens: when the mirror was at rest the two images of the phosphorescent strips were seen in the same straight line, and the adjacent ends of the two images were brought into coincidence by inserting between one of the phosphorescent strips and the mirror a very acute-angled prism. The point of the experiment was to see if the images of the two phosphorescent strips remained in the same straight line when the mirror was in rapid rotation. If, for example, the cathode-rays travelled with the velocity of sound, they would take about  $\frac{1}{3300}$  of a second to pass from one strip to the next; if the mirror were rotating 300 times

a second it would, in the interval taken by sound to pass from one strip to the next, rotate through about  $33^{\circ}$ ; the displacement of the image produced by a rotation one thousandth part of this could easily be detected.

When the phosphorescence was produced by the discharge of an ordinary induction-coil, the images seen in the telescope after reflexion from the revolving mirror were drawn out into very faint ribands of light without definite beginnings or ends; so that it was impossible to say whether or not there was any displacement of one image relative to the other.

I tried a considerable number of phosphorescent substances in the hope of obtaining sharp images, but without success. The substances I tried were ordinary German-glass, uranium-glass, lead-glass, the cyanide of magnesium and platinum, asaron, æsculine, and Schuchardt's "*Leucht-farbe*."

The gradual fading away of the phosphorescence after the exciting cause has been removed, is one reason why one of the edges of the image formed by the revolving mirror should be indistinct: this cannot be remedied unless some substance can be found which ceases to phosphoresce immediately the incidence of the negative rays ceases. I was unable to find any substance possessing this property: of the substances I tried, uranium-glass was the one whose phosphorescence died away most quickly.

I tried several experiments with a specimen of asaron. This substance was found by Lenard to cease to phosphoresce so quickly after the cessation of the phosphorogenic rays that he could not detect its duration in his very sensitive phosphoscope. My specimen of asaron must, I think, have been impure, as it phosphoresced a coral-pink instead of violet as described by Lenard, and its phosphorescence showed a very appreciable duration; in addition to this, it did not give out nearly enough light to be of any use in experiments of this kind.

But even though the images of the phosphorescent strips have one edge (that corresponding to the end of the phosphorescence) indistinct, we can get the information we require about the velocity of the cathode-rays if we can get the image of the edge corresponding to the beginning of the phosphorescence sharp and distinct.

After unsuccessful attempts with several methods, I found that this could be done in the following way, using the oscillatory currents produced by the discharge of a Leyden jar:—The electrodes of the discharge-tube were connected with the ends of the secondary coil of a transformer, whose primary

circuit consisted of a coil of wire with the ends connected to the outside coatings of two Leyden jars, the inside coatings of which were connected with the extremities of an induction-coil: the secondary coil of the transformer had about 30 turns for each turn of the primary coil. It was heavily insulated, and both primary and secondary were immersed in an oil-bath. This transformer easily gave sparks 7 or 8 inches long in air, and when connected to the terminals of a discharge-tube made of uranium-glass produced a very vivid phosphorescence. When the phosphorescence was produced in this way, the images after reflexion in the rotating mirror had one edge quite sharp and distinct, though the other edge was indeterminate in consequence of the duration of the phosphorescence.

When the images of the two bright phosphorescent strips were observed in the telescope, after reflexion from the rapidly revolving mirror, their bright edges were seen to be no longer in the same straight line: if the images came in the field of view from the bottom and went out at the top, then the sharp edge of the phosphorescent strip nearest the electrode was lower than the edge of the other image; if the direction of rotation of the mirror was reversed so that the images came in at the top of the field of view and disappeared at the bottom, then the bright edge of the image of the phosphorescent strip nearest the negative electrode was higher than the bright edge of the image of the other strip. This shows that the luminosity at the strip nearest the cathode begins to be visible before that at the strip more remote; and that the retardation is sufficiently large to be detected by the revolving mirror. This retardation might be explained, (1) by supposing it due to the time taken by the cathode-rays to traverse the distance between the phosphorescent patches; or (2) we might suppose that, though the cathode-rays reached the two phosphorescent patches almost simultaneously, it took longer for the rays falling on the patch at the greater distance from the cathode to raise the patch to luminosity. In other words, there may be an interval between the incidence of the cathode-rays and the emission of the phosphorescent light; this interval being greater the further the phosphorescent patch is from the cathode. This latter supposition cannot, however, explain the displacement of the images for the following reasons:—The sharpness and brightness of the edge of the image show that the phosphorescence, when once it is visible, must attain its maximum brilliancy in a time very small compared with the time taken by the mirror to rotate through an angle large enough to produce the

observed displacement of the images. Again, the two phosphorescent patches are as nearly as possible of equal brightness, so that there can be very little difference in the intensity of the cathode-rays falling upon them : it was for this reason that both the phosphorescent patches were taken some distance down the tube. Again, I took a tube which was bent so that that the cathode-rays fell more directly upon the patch farther from the cathode than upon the other patch, so that in this case the phosphorescence of the more remote patch was brighter. The displacement of the images with this tube was just the same as for the previous, *i. e.* the phosphorescence commenced at the patch nearest the cathode sooner than at the other patch ; whereas if the displacement of the images was due to the interval between the arrival of the rays and the beginning of the phosphorescence it should have commenced at the patch furthest from the cathode, as this was the most exposed to the cathode-rays and phosphoresced with the greatest brilliancy.

I conclude, therefore, that the displacement of the images is due to the time taken by the rays to travel from one patch to the other. This displacement enables us to measure the velocity of the cathode-rays. The amount of displacement observed through the telescope is not constant : even though the mirror is turning at a uniform rate, there are quite appreciable and apparently irregular variations in the amount of the displacement of the images seen in the course of a few minutes. I think these are due to irregularities in the sparks discharging the jar, and the consequent irregularities in the electromotive force acting on the discharge-tube.

When the mirror was rotating 300 times a second, the bright edges of the two patches were on the average separated by the same distance as the image of two lines 1.5 millim. from each other placed against the discharge-tube. Since the distance of the discharge-tube which contained hydrogen from the mirror is 75 centim., the mirror must, in the time taken by the cathode-rays to pass from one patch to the other, have turned through the angle whose circular measure is  $\frac{1.5}{2 \times 750}$ .

Since the mirror makes 300 revolutions per second, the time it takes to rotate through this angle is

$$\frac{1.5}{2 \times 750 \times 2\pi \times 300} = \frac{1}{6\pi \times 10^5} ;$$

and since the distance between the patches is 10 centim., the

velocity of the cathode-rays is

$$6\pi \times 10^6 \text{ cm./sec.},$$

or about

$$1.9 \times 10^7 \text{ cm./sec.}$$

This velocity is small compared with that with which the main discharge from the positive to the negative electrode travels between the electrodes (see J. J. Thomson, Proc. Roy. Soc. 1890). I verified this by inserting an electrode into the far end of the tube used in the previous experiment, and observing the images formed when a bright discharge passed down from the electrode at the beginning to the electrode at the end of the tube. The light from the luminous gas shines through the places where the lampblack has been scraped from the tube, and we get two images, which when the mirror is at rest coincide in position with the images of the two phosphorescent patches in the previous experiment. These images, however, unlike the phosphorescent one, remained in the same straight line when the mirror was rotating rapidly, thus proving that the velocity of the main discharge is very large indeed compared with that of the cathode-rays.

The velocity of the cathode-rays is very much greater than the velocity of mean square of the molecules of gases at the temperature  $0^\circ \text{C}$ . Thus, for example, at  $0^\circ \text{C}$ . the velocity of mean square of the molecules of hydrogen is about  $1.8 \times 10^5$  centimetres per second: the velocity of the cathode-rays is about one hundred times as great. The velocity of the cathode-rays found from the preceding experiments agrees very nearly with the velocity which a negatively electrified atom of hydrogen would acquire under the influence of the potential fall which occurs at the cathode. For, let  $v$  be the velocity acquired by the hydrogen atom under these circumstances,  $m$  the mass of the hydrogen atom,  $V$  the fall in potential at the cathode,  $e$  the charge on the atom; then we have, by the conservation of energy,

$$mv^2 = 2Ve.$$

Now  $e$  has the same value as in electrolytic phenomena, so that  $e/m = 10^4$ .

Warburg's experiments show that  $V$  is about 200 volts, or  $2 \times 10^{10}$  in absolute measure. Substituting this value, we find

$$v^2 = 4 \times 10^{14},$$

or

$$v = 2 \times 10^7 \text{ cm./sec.}$$

A value almost identical with that found by experiment.



The very small difference between the two is of course accidental, as the measurements of the displacement of the images on which the experimental value of  $v$  was founded could not be trusted to anything like 5 per cent.

The action of a magnetic force in deflecting these rays shows, assuming that the deflexion is due to the action of a magnet on a moving electrified body, that the velocity of the atom must be at least of the order we have found.

Consider an atom projected parallel to the axis of the tube which is situated in a uniform field of magnetic force, the lines of magnetic force being at right angles to the axis of the tube. Let  $H$  be the intensity of the magnetic force. Then, if  $m$  is the mass of the atom,  $v$  its velocity, and  $\rho$  the radius of curvature of its path, we have -

$$\frac{mv^2}{\rho} = Hev,$$

where  $e$  is the charge on the atom; since  $e/m$  for hydrogen is  $10^4$ , we have

$$v = \rho H \times 10^4.$$

I cannot find any quantitative experiments on the deflexion of these rays by a magnet; but ordinary observation shows that it would require a strong magnetic field to make  $\rho$  as small as 10 centim., which would mean clearing the tube of phosphorescence except within about 10 centim. of the cathode. If  $v$  were  $2 \times 10^7$ , this would give  $H = 200$ , which is not extravagant.

*XLI. On the Amplitude of Aerial Waves which are but just Audible. By Lord RAYLEIGH, Sec. R.S.\**

**T**HE problem of determining the absolute value of the amplitude, or particle velocity, of a sound which is but just audible to the ear, is one of considerable difficulty. In a short paper published seventeen years ago† I explained a method by which it was easy to demonstrate a superior limit. A whistle, blown under given conditions, consumes a known amount of energy per second. Upon the assumption that the whole of this energy is converted into sound, that the sound is conveyed without loss, and that it is uniformly distributed over the surface of a hemisphere, it is easy to calculate the amplitude at any distance; and the result is necessarily a superior limit to the actual amplitude. In the case

\* Read at the Oxford Meeting of the British Association. Communicated by the Author.

† Proc. Roy. Soc. vol. xxvi. p. 248 (1878).

of the whistle experimented on, of frequency 2730, the superior limit so arrived at for a sound just easily audible was  $8.1 \times 10^{-8}$  cm. The maximum particle velocity  $v$  and the maximum condensation  $s$  are the quantities more immediately determined by the observations, and they are related by the well-known equation  $v = as$ , in which  $a$  denotes the velocity of propagation. In the experiment above referred to the superior limit for  $v$  was .0014 cm. per second, and that for  $s$  was  $4.1 \times 10^{-8}$ . I estimated that on a still night an amplitude, or velocity, one tenth of the above would probably be audible. A very similar number has been arrived at by Wien\*, who used an entirely different method†.

In connection with calculations respecting the sensitiveness of telephones, I was desirous of checking the above estimates, and made some attempts to do so by the former method. In order to avoid possible complications of atmospheric refraction which may occur when large distances are in question, I sought to construct pipes which should generate sound of given pitch upon a much smaller scale, but with the usual economy of wind. In this I did not succeed, and it seems as if there is some obstacle to the desired reduction of scale.

The experiments here to be recorded were conducted with tuning-forks. A fork of known dimensions, vibrating with a known amplitude, may be regarded as a store of energy of which the amount may readily be calculated. This energy is gradually consumed by internal friction and by generation of sound. When a resonator is employed the latter element is the more important, and in some cases we may regard the dying down of the amplitude as sufficiently accounted for by the emission of sound. Adopting this view for the present, we may deduce the rate of emission of sonorous energy from the observed amplitude of the fork at the moment in question and from the rate at which the amplitude decreases. Thus if the law of decrease be  $e^{-\frac{1}{2}kt}$  for the amplitude of the fork, or  $e^{-kt}$  for the energy, and if  $E$  be the total energy at time  $t$ , the rate at which energy is emitted at that time is  $-dE/dt$ , or  $kE$ . The value of  $k$  is deducible from observations of the rate of decay, *e. g.* of the time during which the amplitude is halved. With these arrangements there is no

\* Wied. Ann. xxxvi. p. 834 (1889).

† The first estimate of the amplitude of but just audible sounds, with which I have only recently become acquainted, is that of Toepler and Boltzmann (Pogg. Ann. cxli. p. 321 (1870)). It depends upon an ingenious application of v. Helmholtz's theory of the open organ-pipe to data relating to the maximum condensation within the pipe as obtained by the authors experimentally. The value of  $s$  was found to be  $6.5 \times 10^{-8}$  for a pitch of 181.—August 21.

difficulty in converting energy into sound upon a small scale, and thus in reducing the distance of audibility to such a figure as 30 metres. Under these circumstances the observations are much more manageable than when the operators are separated by half a mile, and there is no reason to fear disturbance from atmospheric refraction.

The fork is mounted upon a stand to which is also firmly attached the observing-microscope. Suitable points of light are obtained from starch grains, and the line of light into which each point is extended by the vibration is determined with the aid of an eyepiece-micrometer. Each division of the micrometer-scale represents  $\cdot 001$  centim. The resonator, when in use, is situated in the position of maximum effect, with its mouth under the free ends of the vibrating prongs.

The course of an experiment was as follows:—In the first place the rates of dying down were observed, with and without the resonator, the stand being situated upon the ground in the middle of a lawn. The fork was set in vibration with a bow, and the time required for the double amplitude to fall to half its original value was determined. Thus in the case of a fork of frequency 256, the time during which the vibration fell from 20 micrometer-divisions to 10 micrometer-divisions was  $16^s$  without the resonator, and  $9^s$  when the resonator was in position. These times of halving were, as far as could be observed, independent of the initial amplitude. To determine the minimum audible, one observer (myself) took up a position 30 yards (27·4 metres) from the fork, and a second (Mr. Gordon) communicated a large vibration to the fork. At the moment when the double amplitude measured 20 micrometer-divisions the second observer gave a signal, and immediately afterwards withdrew to a distance. The business of the first observer was to estimate for how many seconds after the signal the sound still remained audible. In the case referred to the time was  $12^s$ . When the distance was reduced to 15 yards (13·7 metres), an initial double amplitude of 10 micrometer-divisions was audible for almost exactly the same time.

These estimates of audibility are not made without some difficulty. There are usually 2 or 3 seconds during which the observer is in doubt whether he hears or only imagines, and different individuals decide the question in opposite ways. There is also of course room for a real difference of hearing, but this has not obtruded itself much. A given observer on a given day will often agree with himself surprisingly well, but the accuracy thus suggested is, I think, illusory. Much depends upon freedom from disturbing noises. The wind

in the trees or the twittering of birds embarrasses the observer, and interferes more or less with the accuracy of results.

The equality of emission of sound in various horizontal directions was tested, but no difference could be found. The sound issues almost entirely from the resonator, and this may be expected to act as a simple source.

When the time of audibility is regarded as known, it is easy to deduce the amplitude of the vibration of the fork at the moment when the sound ceases to impress the observer. From this the rate of emission of sonorous energy and the amplitude of the aerial vibration as it reaches the observer are to be calculated.

The first step in the calculation is the expression of the total energy of the fork as a function of the amplitude of vibration measured at the extremity of one of the prongs. This problem is considered in § 164 of my 'Theory of Sound.' If  $l$  be the length,  $\rho$  the density, and  $\omega$  the sectional area of a rod damped at one end and free at the other, the kinetic energy  $T$  is connected with the displacement  $\eta$  at the free end by the equation (10)

$$T = \frac{1}{8} \rho l \omega (d\eta/dt)^2.$$

At the moment of passage through the position of equilibrium  $\eta=0$  and  $d\eta/dt$  has its maximum value, the whole energy being then kinetic. The maximum value of  $d\eta/dt$  is connected with the maximum value of  $\eta$  by the equation

$$(d\eta/dt)_{\max.} = 2\pi/\tau \cdot (\eta)_{\max.};$$

so that if we now denote the double amplitude by  $2\eta$ , the whole energy of the vibrating bar is

$$\frac{1}{8} \rho \omega l \pi^2 / \tau^2 \cdot (2\eta)^2,$$

or for the two bars composing the fork

$$E = \frac{1}{4} \rho \omega l \pi^2 / \tau^2 \cdot (2\eta)^2, \quad . \quad . \quad . \quad . \quad (A)$$

where  $\rho \omega l$  is the mass of each prong.

The application of (A) to the 256-fork, vibrating with a double amplitude of 20 micrometer-divisions, is as follows. We have

$$l = 14.0 \text{ cm.}, \quad \omega = .6 \times 1.1 = .66 \text{ sq. cm.}, \\ 1/\tau = 256, \quad \rho = 7.8, \quad 2\eta = .050 \text{ cm.};$$

and thus

$$E = 4.06 \times 10^3 \text{ ergs.}$$

This is the whole energy of the fork when the actual double amplitude at the ends of the prongs is .050 centim.

As has already been shown, the energy lost per second is  $kE$ , if the amplitude vary as  $e^{-\frac{1}{2}kt}$ . For the present purpose  $k$  must be regarded as made up of two parts, one  $k_1$  representing the dissipation which occurs in the absence of the resonator, the other  $k_2$  due to the resonator. It is the latter part only which is effective towards the production of sound. For when the resonator is out of use the fork is practically silent; and, indeed, even if it were worth while to make a correction on account of the residual sound, its phase would only accidentally agree with that of the sound issuing from the resonator.

The values of  $k_1$  and  $k$  are conveniently derived from the times,  $t_1$  and  $t$ , during which the amplitude falls to *one half*. Thus

$$k = 2 \log_e 2 \cdot /t, \quad k_1 = 2 \log_e 2 \cdot /t_1;$$

so that

$$k_2 = 2 \log_e 2 \cdot (1/t - 1/t_1) = 1.386 (1/t - 1/t_1).$$

And the energy converted into sound per second is  $k_2 E$ .

We may now apply these formulæ to the case, already quoted, of the 256-fork, for which  $t=9$ ,  $t_1=16$ . Thus  $t_2$ , the time which would be occupied in halving the amplitude were the dissipation due entirely to the resonator, is 20.6; and  $k_2=.0674$ . Accordingly,

$$k_2 E = 267 \text{ ergs per second,}$$

corresponding to a double amplitude represented by 20 micrometer-divisions. In the experiment quoted the duration of audibility was 12 seconds, during which the amplitude would fall in the ratio  $2^{12/9} : 1$ , and the energy in the ratio  $4^{12/9} : 1$ . Hence at the moment when the sound was just becoming inaudible the energy emitted as sound was 42.1 ergs per second\*.

The question now remains, What is the corresponding amplitude or condensation in the progressive aerial waves at 27.4 metres from the source? If we suppose, as in my former

\* It is of interest to compare with the energy-emission of a source of light. An incandescent electric-lamp of 200 candles absorbs about a horse-power, or say  $10^{10}$  ergs per second. Of the total radiation only about  $\frac{1}{100}$  part acts effectively upon the eye; so that radiation of suitable quality consuming  $5 \times 10^5$  ergs per second corresponds to a candle-power. This is about  $10^4$  times that emitted as sound by the fork in the experiment described above. At a distance of  $10^2 \times 30$ , or 3000 metres the stream of energy from the ideal candle would be about equal to the stream of energy just audible to the ear. It appears that the streams of energy required to influence the eye and the ear are of the same order of magnitude, a conclusion already drawn by Toepler and Boltzmann. —August 21.

calculations, that the ground reflects well, we are to treat the waves as hemispherical. On the whole this seems to be the best supposition to make, although the reflexion is doubtless imperfect. The area  $S$  covered at the distance of the observer is thus  $2\pi \times 2740^2$  sq. centim., and since \*

$$S \cdot \frac{1}{2}apv^2 = S \cdot \frac{1}{2}pa^3s^2 = 42 \cdot 1,$$

we find

$$s^2 = \frac{42 \cdot 1}{\pi \times 2740^2 \times \cdot 00125 \times 34100^3},$$

and

$$s = 6 \cdot 0 \times 10^{-9}.$$

The condensation  $s$  is here reckoned in atmospheres; and the result shows that the ear is able to recognize the addition and subtraction of densities far less than those to be found in our highest vacua.

The amplitude of aerial vibration is given by  $as\tau/2\pi$ , where  $1/\tau = 256$ , and is thus equal to  $1 \cdot 27 \times 10^{-7}$  cm.

It is to be observed that the numbers thus obtained are still somewhat of the nature of superior limits, for they depend upon the assumption that all the dissipation *due to the resonator* represents production of sound. This may not be strictly the case even with the moderate amplitudes here in question, but the uncertainty under this head is far less than in the case of resonators or organ-pipes caused to speak by wind. From the nature of the calculation by which the amplitude or condensation in the aerial waves is deduced, a considerable loss of energy does not largely influence the final numbers.

Similar experiments have been tried at various times with forks of pitch 384 and 512. The results were not quite so accordant as was at first hoped might be the case, but they suffice to fix with some approximation the condensation necessary for audibility. The mean results are as follows:—

$$c', \text{ frequency} = 256, \quad s = 6 \cdot 0 \times 10^{-9},$$

$$c', \quad ,, \quad = 384, \quad s = 4 \cdot 6 \times 10^{-9},$$

$$c'', \quad ,, \quad = 512, \quad s = 4 \cdot 6 \times 10^{-9},$$

no reliable distinction appearing between the two last numbers. Even the distinction between  $6 \cdot 0$  and  $4 \cdot 6$  should be accepted with reserve; so that the comparison must not be taken to prove much more than that the condensation necessary for audibility varies but slowly in the singly dashed octave.

\* 'Theory of Sound,' § 245.

XLII. *Note on the Relation between the Coefficients of Pressure in Thermometry.* By C. CHREE, M.A.\*

THE study of thermometers intended for very exact physical work has been the object of much patient research at the Bureau International des Poids et Mesures, and an important book†, embodying the principal results obtained and giving a full account of the several corrections required, has been written by Dr. Guillaume, attaché to the Bureau. The present paper was called into existence by Dr. Guillaume's discussion on his pages 99–111 of what he terms "Coefficients de Pression."

There are two such coefficients of pressure, an "external" and an "internal." Both have to do with the change in the internal volume of the thermometer, *i. e.* the volume contained within the inner glass surface; but the external coefficient is connected with the reduction of this volume under increased pressure on the outside of the thermometer, while the internal coefficient is connected with the increase of volume accompanying increased pressure on the inner surface itself.

The increase of external pressure may be due to a rise in the barometer or to immersion in a liquid; while an increased internal pressure follows a rise in temperature if the stem be vertical, or the alteration of the thermometer from a horizontal to a vertical position.

As a matter of convenience, Dr. Guillaume combines the correction required by the change of volume of the glass with that required by the compressibility of the mercury itself. Here, however, we shall have to do solely with the corrections due to the compressibility of the glass. The coefficients of pressure dealt with here are those which Dr. Guillaume (*l. c.* p. 99) denotes by the letters  $\alpha_i$  and  $\alpha_e$ . They may be defined as follows:—

Let  $V_i$  denote the internal volume of the thermometer when free from all pressure. Let this become increased by  $\delta V_i'$  when there is a uniform internal pressure  $p'$  and no external pressure, and let it become diminished by  $\delta V_i''$  when there is a uniform external pressure  $p''$  and no internal

\* Communicated by the Author.

† *Traité Pratique de la Thermométrie de Précision.* (Gauthier-Villars et Fils, Paris, 1889.)

pressure ; then

$$\alpha_i = \frac{1}{p'} \frac{\delta V'_i}{V_i}, \quad . . . . . (1)$$

$$\alpha_e = \frac{1}{p''} \frac{\delta V''_i}{V_i}. \quad . . . . . (2)$$

It is assumed that the change of volume does not exceed the elastic limits, and that strain varies directly as stress ; in other words, that  $\alpha_i$  and  $\alpha_e$  are constants independent of the absolute magnitude of  $p'$  or  $p''$ .

The experimental determination of  $\alpha_e$  appears to be easy ; but that of  $\alpha_i$  is, according to Dr. Guillaume, so troublesome\* that he prefers to deduce it by the theoretical relation

$$\alpha_e - \alpha_i = 1/k, \quad . . . . . (3)$$

where  $k$  is the bulk-modulus of glass, assumed to be an isotropic elastic material.

On reading Dr. Guillaume's book I was struck by the simplicity of the result (3), but was unable to feel confidence in the proof, of which the following is a brief outline:—

Let  $R_i$  and  $R_e$  denote the radii of the inner and outer surfaces of an isotropic spherical shell, and let it become exposed to uniform internal and external pressures  $P_i$  and  $P_e$ . Then the elastic displacement  $u$  is along the radius, and is given at a distance  $r$  from the centre by

$$u = \frac{1}{3\lambda + 2\mu} \frac{P_i R_i^3 - P_e R_e^3}{R_e^3 - R_i^3} r + \frac{1}{4\mu} \frac{(P_i - P_e) R_e^3 R_i^3}{R_e^3 - R_i^3} \frac{1}{r^2}, \quad . . . (4)$$

where  $\lambda$  and  $\mu$  are Lamé's elastic constants. Noticing

$$k = \lambda + \frac{2}{3}\mu,$$

it is easy to prove that the relation (3) holds exactly.

Take next a hollow circular cylinder extending from the plane  $z=0$  in the direction of  $z$  positive. Let  $R_i$  and  $R_e$  be the radii of its inner and outer cylindrical boundaries, and let uniform internal and external pressures  $P_i$  and  $P_e$  be applied. Then, according to Dr. Guillaume, there is at any point not too near the ends of the cylinder, and at distance  $r$  from the axis, a displacement  $w$  parallel to the axis and a displacement

\* See, however, vol. i. p. 79 of the *Wiss. Abhand. Physik. Tech. Reichsanstalt* at Charlottenburg, with description of the direct determination of the internal coefficient and results.



$u$  perpendicular to it given by

$$\left. \begin{aligned} w &= \frac{1}{3\lambda + 2\mu} \frac{P_i R_i^2 - P_e R_e^2}{R_e^2 - R_i^2} z, \\ u &= \frac{1}{3\lambda + 2\mu} \frac{P_i R_i^2 - P_e R_e^2}{R_e^2 - R_i^2} r + \frac{1}{2\mu} \frac{P_i - P_e}{R_e^2 - R_i^2} \frac{R_i^2 R_e^2}{r} \end{aligned} \right\} . \quad (5)$$

If we now suppose (5) to apply throughout the *whole* length  $Z$  of the cylinder, whose internal volume is  $\pi R_i^2 Z$ , we again find the relation (3) to hold.

Having proceeded thus far Dr. Guillaume argues as follows \*:—"En supposant, ce qui n'est sans doute qu'approximativement vrai, que, dans un réservoir composé d'un cylindre terminé par des hémisphères, la partie cylindrique et les calottes se déforment d'une manière indépendante, on pourra combiner les formules précédentes de façon à obtenir les valeurs qui conviennent sensiblement au cas d'un réservoir thermométrique. La relation (3), commune aux deux cas, doit encore subsister."

In order to judge of the force of the concluding argument we must consider what has been actually proved. The solution (4) is quite satisfactory for a uniform isotropic material bounded by two complete, exactly concentric, spherical surfaces. The solution (5) gives a uniform pressure  $P_i$  over the inner surface  $r = R_i$ , and a uniform pressure  $P_e$  over the outer surface  $r = R_e$  of a cylindrical tube of isotropic material; it likewise gives a resultant tension  $\pi(P_i R_i^2 - P_e R_e^2)$  uniformly distributed over the area  $\pi(R_e^2 - R_i^2)$  of any section perpendicular to the axis of the tube.

Now if we supposed a hollow vessel constructed of the cylindrical tube in question closed at each end by any form of surface, or *cap*, to be exposed to uniform internal and external pressures  $P_i$  and  $P_e$ , the resultant of the pressures on one of the caps is necessarily a force  $\pi(P_i R_i^2 - P_e R_e^2)$  parallel to the axis, and by ordinary statics this must equal the resultant of the tensions over any orthogonal cross section of the tube. With a cap symmetrical about the axis of the cylinder, the tension borne by the wall of the tube will obviously be the same at all points in the same transverse section which are equidistant from the axis. The solution (5) would thus satisfy all the conditions for the cylindrical portion of the hollow vessel if the caps were of such a form that the tensions parallel to the axis of the cylinder over the transverse sections where the cylindrical wall passes into the caps

\* *Loc. cit.* p. 102.

were independent of  $r$ . This, however, is not the case for either hemispherical or plane caps, and it is open to doubt whether it can be secured by caps of any form. The solution (5) thus breaks down in this respect. In accordance, however, with what has been termed the "equivalence of statically equipollent systems of terminal loading"\* , it is pretty generally conceded that if one dimension of a body be relatively small, such as the diameter of a long beam, then the precise law of distribution of forces applied over the small dimension is not of great importance so far as concerns the elastic strains and stresses, except at points near the surface where the force is applied. It would thus, I think, be generally admitted that, in the case of a closed tube of length not less than twenty times its external diameter, (5) would apply in the case of uniform pressures with a close approach to accuracy throughout much the greater portion of the volume. At the same time it is uncertain how large are the terminal volumes throughout which (5) is appreciably erroneous, and how great is the effect of the consequent error on the result (3). This error is really neglected by Dr. Guillaume, for though he starts by admitting the failure of (5) near the ends of the tube he applies it finally to the entire length.

A more serious objection arises when we pass to the assumption that (4) holds for two hemispherical caps connected by a cylindrical tube. Let us lay aside for the moment any preconceived ideas as to the shape of a thermometer, and suppose we are really dealing with a cylindrical tube with hemispherical ends, whose radii  $R_i$ ,  $R_e$  are the same as the cylinder's. In this case the theory of equipollent systems of loading cannot be invoked with the least show of reason, so far as the hemispheres are concerned, unless the thickness  $R_e - R_i$  of material be very small compared to  $R_i$ ; and even in that extreme shape the error introduced by applying the theory would be most uncertain. There is thus, I think, very little mathematical basis for the assumption that (4) may be applied to two hemispheres connected by a cylindrical tube, unless it should turn out that the solutions (4) and (5) are in very close agreement over the transverse sections where the hemispherical caps pass into the cylindrical tube. This, however, is in general far from the case. We see in fact that the radial displacements  $u$  in (4) and in (5) are totally different functions of  $r$ , except in the special case when  $P_i = P_e$ . A like incompatibility will be found between the stress parallel to the axis in the cylinder and the stress it would require to equal in the hemisphere.

\* See Todhunter and Pearson's 'History of Elasticity,' vol. ii. art. 21.

There is a final objection to the extension of the result (3) to a thermometer, which has doubtless occurred already to every one familiar with the ordinary shape of that instrument. A mercury-thermometer of ordinary dimensions which makes the slightest pretence to an open scale must have the internal diameter of its bulb a very large multiple of that of its tube. Its resemblance to a cylindrical tube with hemispherical ends, whose diameters must of course equal that of the tube, is thus so remote that even if (3) had been satisfactorily established for the one body its extension to the other would have been a very long step into the unknown.

The object of the preceding remarks is solely to show the necessity for further investigation. It is far from my desire to reflect in any way on the author of the proof, whether Dr. Guillaume or another. The discriminating physicist whom the exigencies of the case compel to use imperfect mathematical methods, but who nevertheless reaches results of practical utility, ought not to be classed with the mathematical proficient who overlooks errors in his analysis which wholly vitiate his physical conclusions, or who fails to recognize fundamental differences between the problem he has actually solved and that which is presented by nature. While the mathematician devoid of physical insight may go badly wrong through some slip which mathematically considered is insignificant, the man possessed of keen physical instincts would almost appear protected by a special providence which causes even his mistakes to work to his advantage.

The conclusion to which my own investigations lead is that, *on the hypothesis of uniform pressure, (3) is true absolutely, and not merely approximately, for any homogeneous elastic material, isotropic or aeolotropic, limited by an internal and an external surface of any shape or shapes whatsoever; and this I now proceed to prove.*

In any homogeneous elastic material, with any number of elastic constants from 2 to 21, acted on only by surface-forces, the elastic stresses must satisfy the three internal equations

$$\left. \begin{aligned} \frac{d \widehat{xx}}{dx} + \frac{d \widehat{xy}}{dy} + \frac{d \widehat{xz}}{dz} &= 0, \\ \frac{d \widehat{xy}}{dx} + \frac{d \widehat{yy}}{dy} + \frac{d \widehat{yz}}{dz} &= 0, \\ \frac{d \widehat{xz}}{dx} + \frac{d \widehat{yz}}{dy} + \frac{d \widehat{zz}}{dz} &= 0, \end{aligned} \right\} \quad \dots \dots (6)$$

where we employ the symmetrical notation of Todhunter and Pearson's 'History,' and refer everything to fixed Cartesian axes. Also if  $\lambda'$ ,  $\mu'$ ,  $\nu'$  denote the direction-cosines of the outward-drawn normal at any point on a surface, and  $F$ ,  $G$ ,  $H$  be the components of the applied force there per unit area of surface, we must have

$$\left. \begin{aligned} \lambda' \widehat{xx} + \mu' \widehat{xy} + \nu' \widehat{xz} &= F, \\ \lambda' \widehat{xy} + \mu' \widehat{yy} + \nu' \widehat{yz} &= G, \\ \lambda' \widehat{xz} + \mu' \widehat{yz} + \nu' \widehat{zz} &= H. \end{aligned} \right\} \dots \dots \dots (7)$$

The internal equations are obviously satisfied by

$$\left. \begin{aligned} \widehat{xy} = \widehat{yz} = \widehat{xz} &= 0, \\ \widehat{xx} = \widehat{yy} = \widehat{zz} &= -p, \end{aligned} \right\} \dots \dots \dots (8)$$

where  $p$  is any constant.

If the material be bounded by one surface  $S_e$ , this is obviously the solution for a uniform pressure  $p$  over that surface, for the components of  $p$  are

$$\left. \begin{aligned} F &= -\lambda' p, \\ G &= -\mu' p, \\ H &= -\nu' p, \end{aligned} \right\} \dots \dots \dots (9)$$

so that the equations (7) are satisfied.

Answering to (8) we have everywhere a uniform "dilatation"  $\Delta$  given by

$$\Delta = -p/k, \dots \dots \dots (10)$$

where  $k$  is the bulk-modulus\*.

As  $\Delta$  is uniform, the reduction  $\delta V_e$  of the volume  $V_e$  enclosed by  $S_e$  is given by

$$\delta V_e / V_e = -\Delta = p/k,$$

and so

$$\frac{1}{p} \frac{\delta V_e}{V_e} = \frac{1}{k}. \dots \dots \dots (11)$$

Suppose, now, any imaginary surface  $S_i$  drawn in the material enclosing a volume  $V_i$ . Then since (8) holds everywhere, it holds over the surface  $S_i$ , and so glancing at (7) we recognize that the stress over  $S_i$  is a uniform normal pres-

\* See Thomson and Tait's 'Natural Philosophy,' Part ii. art. 682, and Love's 'Elasticity,' vol. i. art. 41.

sure  $p$ . Thus in a shell bounded by  $S_i$  and  $S_e$  under *equal* uniform pressures  $p$  on the two surfaces, the stresses, and so the strains and displacements, are at every point the same as if  $S_i$  were an imaginary surface drawn in material completely filling  $S_e$ , and  $p$  were applied over  $S_e$  only. In particular, the changes in the volumes contained by the surfaces  $S_i$  and  $S_e$  must be the same in the two cases.

In the case of the shell, let  $\delta V'_i$  and  $\delta V'_e$  be the increases in the volumes  $V_i$  and  $V_e$  when uniform pressure  $p$  is applied over the inner surface only, and let  $\delta V''_i$  and  $\delta V''_e$  be the corresponding reductions when the same pressure  $p$  is applied over the outer surface only.

In the case of the solid, bounded by the one surface  $S_e$ , let  $\delta V_i$  be the reduction in the partial volume  $V_i$ , and  $\delta V_e$  the reduction in the total volume  $V_e$  due to uniform pressure  $p$  over  $S_e$ . Then by what has preceded, since stresses are superposable,

$$\delta V''_i + (-\delta V'_i) = \delta V_i, \quad . \quad . \quad . \quad . \quad (12)$$

$$\delta V''_e + (-\delta V'_e) = \delta V_e. \quad . \quad . \quad . \quad . \quad (13)$$

But in the case of the complete solid  $\Delta$  is uniform, being given by (10), and so

$$\frac{1}{p} \frac{\delta V_i}{V_i} = \frac{1}{p} \frac{\delta V_e}{V_e} = \frac{1}{k}. \quad . \quad . \quad . \quad . \quad (14)$$

Thus, substituting for  $\delta V_i$  in (12), we get

$$\frac{1}{p} \frac{\delta V''_i}{V_i} - \frac{1}{p} \frac{\delta V'_i}{V_i} = \frac{1}{k}; \quad . \quad . \quad . \quad . \quad (15)$$

or, after Dr. Guillaume's definition, see (1) and (2),

$$\alpha_e - \alpha_i = \frac{1}{k},$$

the result required.

Again substituting for  $\delta V_e$  from (14) in (13), we get

$$\frac{1}{p} \frac{\delta V''_e}{V_e} - \frac{1}{p} \frac{\delta V'_e}{V_e} = \frac{1}{k}. \quad . \quad . \quad . \quad . \quad (16)$$

Dr. Guillaume had no occasion to arrive at this latter result. To put it in a similar form to the other, let  $\gamma_i$  represent the increase per unit volume of  $V_e$  due to unit pressure per unit surface of  $S_i$ , and let  $\gamma_e$  represent the reduction per

unit volume of  $V_e$  due to unit pressure per unit surface of  $S_e$ , then

$$\gamma_i = \frac{1}{p} \frac{\delta V'_e}{V_e}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\gamma_e = \frac{1}{p} \frac{\delta V''_e}{V_e}; \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and so by (16),

$$\gamma_e - \gamma_i = \frac{1}{k}. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Since the result (3) may come under the notice of some persons whose interest in thermometry is not accompanied by a knowledge of elastic solids, it may be well to state explicitly under what conditions it has been proved to hold, and wherein these conditions may differ from what occurs in practice with actual thermometers.

The conditions assumed in the mathematical theory are :—

- (A) that the material is completely homogeneous, though not necessarily isotropic ;
- (B) that the pressure is perfectly uniform over the surface where it is applied ;
- (C) that the volume whose change is considered is the entire volume within the inner surface.

The fact that (3) holds when all these conditions are satisfied does not of course necessarily imply that it ceases to hold if one of the conditions is not satisfied. As a matter of fact it certainly holds in one case when (A) is only partially satisfied, viz. in the case of a spherical shell composed of concentric layers of different isotropic materials, which though differing in rigidity have all the same compressibility. But it is obvious that in any case where the compressibility, and so the bulk-modulus, is not uniform it would be meaningless.

There is room for doubt as to how far condition (A) is satisfied by thermometers. Differences of elastic quality between the bulb and stem, or even between the material at the outside and inside of the stem, seem not unlikely to occur.

The condition (B) is probably never satisfied exactly; and it may be very far from holding when the stem is vertical, in the case either of internal pressure or external fluid pressure. It may, however, be regarded as practically satisfied in the case of external atmospheric pressure.

The preceding mathematical theory gives no direct and certain information as to how the change of volume is divided between the bulb and stem even when the pressure is uniform. If, however, we for a moment supposed the bulb and a short

adjacent portion of the stem to be converted into a closed vessel by means of a flat disk of glass closing the bore, the effect on the change of the volume so enclosed could hardly differ appreciably from that occurring previous to the closure, supposing the bore to be fine. Also if the bulb be nearly spherical the pressure over its surface would seem, so far as change of volume is concerned, to be replaceable without serious error by a uniform pressure equal to that actually found at the level of the bulb's centre.

We should thus conclude that the change in the volume of a nearly spherical bulb follows approximately the same law as if the bulb were closed and subjected to uniform pressure equal in intensity to that occurring at the level of its centre of gravity. A relation equivalent to (3) thus seems likely to hold approximately for the bulb alone, at least when it is nearly spherical and the bore is fine. This is, I think, practically in harmony with the conclusion reached by Dr. Guillaume on his p. 111.

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*XI.III. On a New Method for Mapping the Spectra of Metals.*  
By Prof. HENRY CREW and Mr. ROBERT TATNALL\*.

THE difference in physical character between the various lines in the spectrum of an element has recently assumed such importance that a table of wave-lengths is now, to some extent, incomplete unless accompanied by a photographic map. This is especially true for one who is seeking new relations among the wave-lengths. Thus, in the case of cadmium, the triplets overlap, but, "owing to the *physical similarity* of the lines forming any one triplet, it is a matter of perfect ease to select them"†.

Indeed, in many cases where series have been discovered, one might decide to what series a given line belongs quite as well by its appearance as by its wave-length. Rydberg has happily suggested, for these series, names which describe the appearance of their respective lines.

So far as we are aware, all photographs of metallic spectra which have hitherto been made are, with two exceptions, either of spark spectra or spectra of substances vaporized in the carbon arc. The two exceptions to which we refer are, *first*, the well-known spectrum of iron by Kayser and Runge, in which the arc employed is that between iron rods about one centim. in diameter; and, *secondly*, a copper arc with

\* Communicated by the Authors.

† Ames, Phil. Mag. July 1890, p. 45.

which these same gentlemen have attempted to vaporize strontium, and thus obtain the strontium triplet\* at  $\lambda 3800$ , free from the cyanogen band. They say, however, that the arc worked so badly as to give only one line out of the three.

The well-known difficulty with the spark spectrum is that it is almost as characteristic of the slight differences in physical condition under which it is obtained as of the chemical element from which it is obtained. Not only so, but owing to its streaks, as it were, of high temperature ("luminescence"?) there is obtained, at the same time with the spectrum of the metal, also the spectra of the gases in which the discharge takes place.

In the case of the carbon arc, nature has fortunately grouped its many thousand lines into bands, leaving here and there comparatively clear spaces in which the lines due to substances deliberately introduced into the arc can be studied and measured with a high degree of accuracy, as exemplified in the work of Rowland and of Kayser and Runge.

Fortunately also, in the case of some metals, especially the easily volatile ones, the metallic vapour acts *as if* it shunted off the current from the carbon vapour; and the metal comes out strong in comparison with the carbon.

At the same time, the carbon and cyanogen bands stretch practically through the whole spectrum from  $\lambda 3500$  into the infra-red. Not only so, but many of these carbon lines have, as a rule, intensities quite comparable to those of the metallic lines. One ingenious effort has been made by Kayser and Runge (*l. c.*) to rid themselves of the cyanogen bands by working the carbon arc in a current of carbon dioxide. This is partially successful; but, at best, it only diminished the intensity of the band. Messrs. Lewis and Ferry†, speaking of the infra-red spectra of the metals, say:—"It seems as though little more could be done in the discovery of new metallic lines unless the carbon lines are first carefully mapped, or some means is devised for raising the substances investigated to sufficiently high temperature without placing them directly in the [carbon] arc."

We have, therefore, devised and used during the past year the following method for obtaining the arc spectrum of the metallic elements free from carbon, free from air-lines, and free also from any continuous spectrum.

The idea is simply that of an arc in which one pole rapidly

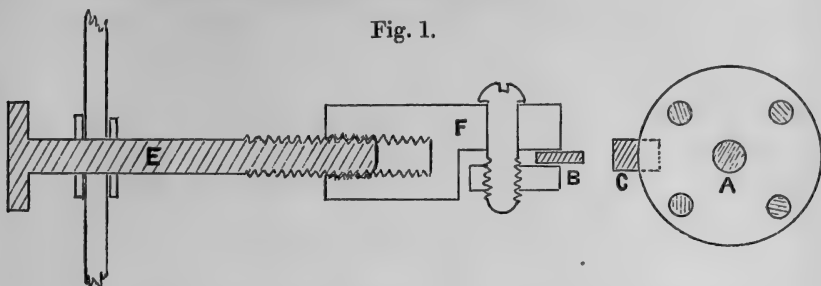
\* Kayser and Runge, Wied. *Ann.* lii. p. 115 (1894).

† Johns Hopkins University Circular, May 1894.



rotates or vibrates, thus preventing welding and destroying the coating of oxide which in some cases interrupts the current between ordinary metallic poles.

Fig. 1.



To accomplish this, a brass disk is fitted, by means of a collar and set-screw, to the shaft (or counter-shaft) of a small high-speed electric motor. Parallel to this brass disk, and upon it as a base, is screwed a similar disk. These disks are used as jaws in which to clamp small pieces of metal to be vaporized. One pole of the electric circuit which includes the arc is connected, by brushes, to the counter-shaft, shown in section at A (fig. 1). The other pole of the arc circuit is connected to another clamp F, which, by means of the screw E, can be made to approach or recede from the rotating disk. The clamp F is also fitted with parallel jaws, to receive a small piece of the metal (B) to be vaporized. This metal B is moved always parallel to itself, and the arc between B and C is maintained always at the same point. Both the rotating and the sliding jaws are mounted on the same base with the motor; and the whole is so light as to be easily carried about in one hand.

The disk is set in rapid rotation and the metal at B is slowly fed in, by the screw E, until the arc strikes. The incandescent vapour is then carried out by the disk into the form of an open fan, and is projected upon the slit of the spectro-scope by the "image" lens.

In the case of those elements which are easily obtainable in the form of a regulus, an entire disk may be made of the metal. With the rarer elements one needs to use only a small piece in the clamp, but the time of exposure is correspondingly lengthened. The disk once started, no attention is required except the feeding-in of the metal, B. Nearly all the wear is on this piece and very little on the disk, so that the latter will last for a comparatively long time, while the former has to be renewed with a frequency depending upon the amount of current employed. We have generally used

a hundred-volt circuit and an alternating current of from two to ten amperes. Higher voltages sustain a longer arc, and thus protect the metal from mechanical wear.

For the purpose of a comparison spectrum is used a second counter-shaft placed parallel to, and in the same horizontal plane with, the first. This shaft carries an iron disk, about an inch in diameter, against which is fed a piece of iron tubing. The spectrum of any one metal having been photographed, the whole instrument is translated laterally and the current switched on to the iron disk. While not so convenient as the sun in many ways, the iron spectrum has an abundance of sharp lines evenly distributed: it permits one to work in all kinds of weather and at night.

The plates whose measures follow will illustrate the method. They were taken with a Rowland concave grating of ten feet radius and ruled with fifty thousand lines. The portion of the plate measured, in each case, covers a part of the spectrum where the carbon bands are strong. Knowing of no adequate method of reproduction, except silver printing, which is too expensive, we have selected three typical plates and simply measured on a dividing-engine all the lines visible, including "ghosts" and recognized impurities. The tables explain themselves. They include all the lines certainly visible through the reading-microscope of the dividing-engine; but a still lower-power microscope shows a number of weaker lines between those measured. The wave-lengths were determined not with the highest accuracy possible, but well within a tenth of an Ångström unit, which is usually ample for purposes of identification. The method was interpolated between two of Rowland's standard iron lines, except in the case of copper, where, for convenience, the interpolation is between two of Kayser and Runge's copper lines.

Plate No. 178. *Tin.*

Element.	Plate 178.	Kayser and Runge.	Remarks.
Tin .....	(4893·66)	3262·44	{ Third order line: not completely absorbed by glass.
Tin .....	(4762·72)	3175·12	
(Ghost)...	4531·20	.....	" " " " " Sn 4524·92."
(Ghost) ...	4528·04	.....	First order ghost of Sn 4524·92.
Tin .....	4524·91	4524·92	Intensity 2.
(Ghost) ...	4521·77	.....	First order ghost of Sn 4524·92.
(Ghost) ...	4518·63	.....	Second order ghost of Sn 4524·92.
	4511·43	.....	Intensity 6; sharp.

Plate 177. *Copper.*

Element.	Plate 177.	Kayser and Runge.	Intensity.	Remarks.
Copper ...	4003·18	4003·18	5	
	3998·08	.....	6	Hazy.
	3979·97	.....	6	Hazy.
	3976·14	.....	6	Extremely wide and hazy.
Calcium ...	3968·55	.....	4	Fraunhofer's H.
	3964·27	.....	6	Wide and hazy.
	3961·64	.....	6	Very weak.
	3951·63	.....	6	Very weak.
	3947·00	.....	6	Hazy.
Calcium ...	3933·76	.....	4	Fraunhofer's K.
	3933·11	.....	6	Wide and hazy.
Copper ...	3925·36	3925·40	5	
Copper ...	3821·32	3821·38	5	
Copper ...	3899·42	3899·43	6	
	3888·73	.....	6	{ Very weak and hazy; caesium line at $\lambda$ 3888·83.
	3883·39	.....	6	{ No resemblance to head of C band at 3883·47.
	3881·75	.....	6	Hazy.
(Ghost) ...	3865·97	.....	...	Second order; belongs to Cu 3860·64.
Copper ...	3861·90	3861·88	5	
Copper ...	3860·57	3860·64	2	
Iron .....	3860·03	.....	6	Fe 3860·03 (K. & R.).
(Ghost) ...	3857·88	.....	6	First order; belongs to Cu 3860·64.
	3844·57	.....	6	Wide and hazy.
	3837·48	.....	6	Wide and hazy.
Iron .....	3825·99	.....	6	Sharp trace of Fe 3826·04 (K. & R.).
Copper ...	3825·17	3825·13	6	
Copper ...	3820·97	3821·01	4	
	3820·52	.....	6	Sharp; unlike Hg 3820·6 (K. & R.).
	3817·57	.....	6	Hazy.
	3813·60	.....	5	Probably not copper.
Copper ...	3812·08	3812·08	6	Wide and hazy.
Copper ...	3805·29	3805·33	3	
	3803·64	.....	6	Wide and hazy.
	3800·57	.....	4	Fairly sharp.
	3799·99	.....	5	Rather sharp.
	3797·34	.....	6	Hazy.
	3785·74	.....	6	Wide and hazy.
	3780·20	.....	6	Wide and hazy.
Copper ...	3771·96	3771·96	4	
	3764·98	.....	6	Wide and hazy.
Copper ...	3759·56	3759·53	4	
Iron .....	3758·36	.....	6	Fe 3758·36 (K. & R.).
Iron .....	3749·61	.....	6	Fe 3749·61 (K. & R.).
	3745·53	.....	5	Hazy.
	3743·53	.....	6	
Copper ...	3741·36	3741·32	3	
Iron .....	3737·27	.....	6	Fe 3737·27 (K. & R.).
Iron .....	3734·96	.....	6	Sharp trace of Fe 3735·00 (K. & R.).
Copper ...	3734·29	3734·27	3	

Plate 177. *Copper (continued).*

Element.	Plate 177.	Kayser and Runge.	Intensity.	Remarks.
	3721·79	.....	6	Hazy.
	3720·89	.....	5	Very sharp.
	3720·09	.....	6	Sharp.
Copper ...	3712·06	3712·05	4	Hazy.
	3707·31	.....	6	Exceedingly weak and hazy.
Iron .....	3701·20	.....	6	Trace of Fe 3701·20 (K. & R.).
Copper ...	3700·61	3700·63	3	
	3699·17	.....	6	Hazy.
	3695·48	.....	6	Hazy.
Copper ...	3688·38	3688·60	6	Exceedingly wide and hazy.
	3686·67	.....	5	Rather sharp.
	3685·04	.....	6	Rather sharp.
Copper ...	3684·77	3684·75	3	
Lead .....	3683·60	.....	6	Faint trace of Pb 3683·60 (K. & R.).
Copper ...	3676·96	3676·97	5	
Copper ...	3672·04	3672·00	5	
Copper ...	3665·83	3665·85	4	
	3664·21	.....	6	Hazy.
Copper ...	3659·44	3659·44	5	
Copper ...	3656·86	3656·90	6	
Copper ...	3655·99	3655·99	4	
Copper ...	3654·47	3654·6	6	
Copper ...	3652·48	3652·56	6	
	3650·97	.....	6	Hazy.
Copper ...	3648·52	3648·52	5	
Copper ...	3645·31	3645·32	4	
*	3643·80	.....	6	
Copper ...	3641·80	3641·79	5	
Copper ...	3636·01	3636·01	4	
	3632·67	.....	5	Shaded towards violet.
	3629·90	.....	6	
Copper ...	3627·40	3627·39	4	
Copper ...	3624·36	3624·35	5	
Copper ...	3621·32	3621·33	3	
Copper ...	3620·47	3620·47	5	
	3619·52	.....	6	Certainly not copper.
(Ghost) ...	3618·88	.....	6	First order: belongs to Cu 3621·33.
(Ghost) ...	3616·37	.....	6	Second " " "
Copper ...	3614·31	3614·31	6	
Copper ...	3613·85	3613·86	4	
	3610·88	.....	5	Hazy. Strong Cd line at $\lambda$ 3610·66.
	3609·43	.....	5	Very sharp.
(Ghost) ...	3607·22	.....	6	Second order: belongs to 3602·11.
(Ghost) ...	3604·64	.....	6	First " " "
(Ghost) ...	3604·30	.....	6	Second " " "
Copper ...	3602·10	3602·11	3	
Copper ...	3599·20	3599·20	3	

\* The iron line at 3643·80 (K. & R.) is much weaker than some of its neighbours which do *not* show as impurity lines. Hence this line is probably not iron.

Plate 169. *Zinc.*

Element.	Plate 169.	Kayser and Runge.	Remarks.
(Ghost) .....	4828·26	.....	Fifth order.
" .....	4824·21	... ..	Fourth "
" .....	4821·10	.....	Third "
" .....	4817·41	.....	Second "
" .....	4814·18	.....	First "
Zinc .....	4810·79	4810·71	Intensity 1.
(Ghost) .....	4807·36	.....	First order.
" .....	4804·11	.....	Second "
" .....	4800·84	.....	Third "
" .....	4797·30	.....	Fourth "
" .....	4793·99	.....	Fifth "
" .....	4788·70	.....	Fifth "
" .....	4735·52	.....	Fourth "
" .....	4732·26	.....	Third "
" .....	4728·89	.....	Second "
" .....	4725·70	.....	First "
Zinc .....	4722·34	4722·26	Intensity 1.
(Ghost) .....	4719·03	.....	First order.
" .....	4715·79	.....	Second "
" .....	4712·67	.....	Third "
" .....	4709·36	.....	Fourth "
" .....	4705·98	.....	Fifth "
" .....	4693·27	.....	Fourth "
" .....	4686·85	.....	Second "
" .....	4683·50	.....	First "
Zinc .....	4680·38	4680·38	Intensity 1.
(Ghost) .....	4677·04	.....	First order.
" .....	4673·97	.....	Second "
" .....	4670·66	.....	Third "
" .....	4667·52	.....	Fourth "
" .....	4664·26	.....	Fifth "
Zinc .....	4630·06	4630·06	Intensity 4.
Zinc .....	(4613·96)	3075·99	Intensity 6: Third order line.
Zinc .....	(4608·29)	3072·19	" " "
Zinc .....	(4553·83)	3035·93	" " "

Out of 98 lines measured on the copper plate, it will be noticed that we are unable to identify 41. They are not to be found among Kayser and Runge's values for Ag, Au, Sn, Pb, As, Sb, Mg, Ca, Zn, Sr, Cd, Ba, Hg, Li, Na, K, Rb, Cs, or Fe.

It is probable that these 41 lines belong to impurities whose wave-lengths have not yet been determined (or, at least, not published) with an accuracy sufficient for identification. It is not impossible, however, that some of these are *new* copper lines. We have found very little difference between "com-

mercial" copper and that which is sold by chemical supply houses under the label "chemically pure."

From the tables it will be seen that the plates are practically clear except for the impurity lines, which are very weak, many of them not showing on a silver print. In any case a table of the impurity lines and "ghosts" might accompany each map. A few years hence, when the spectra of the metals are more completely measured, such a table will be easily made.

North-Western University,  
Evanston, Illinois, U.S.A.  
July, 1894.

XLIV. *On the Vibrations of a Loaded Spiral Spring.* By  
L. R. WILBERFORCE, M.A., *Demonstrator in Physics at the  
Cavendish Laboratory, Cambridge*.\*

IT has been pointed out by Profs. Ayrton and Perry† that, by comparing the axial elongation and the twisting produced in a spiral spring of finite angle by the action of an axial force, we can deduce the ratio of the torsional and flexural rigidities of the wire or strip of which the spring is made, and hence obtain the ratio of the rigidity to the Young's modulus of its material.

This method is very interesting and instructive; but as it is not easy to produce springs of convenient and yet sufficiently uniform angles, nor to determine accurately a small axial elongation, it seemed to me that it might be worth while to modify it by attaching a mass to the spring and observing the periods of the vibrations which it executes when displaced. In this case it will be found convenient to use a spring of an angle so small that its square may be neglected.

Apart from their use in comparing moduli of elasticity, the vibrations of such a system present some rather interesting features, of which a detailed consideration may not be out of place.

If we have a spiral spring made of a length  $l$  of wire, and wound on a cylinder of radius  $r$ , so that the distance between the ends of the spring is  $x$ , and if  $\phi$  is the angle between the planes through the axis of the spiral and the two ends of the wire, the force and couple required to produce a deformation from the equilibrium state ( $x_0, \phi_0$ ) to the state

\* Communicated by the Author.

† Proc. Roy. Soc. vol. xxxvi. p. 311.

( $x, \phi$ ) are respectively given by\*

$$F_{x, \phi} = -\frac{B}{l^3} \{ \sqrt{l^2 - x^2} \phi - \sqrt{l^2 - x_0^2} \phi_0 \} \frac{x\phi}{\sqrt{l^2 - x^2}} + \frac{A}{l^3} (x\phi - x_0\phi_0) \phi,$$

$$C_{x, \phi} = \frac{B}{l^3} \{ \sqrt{l^2 - x^2} \phi - \sqrt{l^2 - x_0^2} \phi_0 \} \sqrt{l^2 - x^2} + \frac{A}{l^3} (x\phi - x_0\phi_0) x,$$

where  $A$  is the torsional and  $B$  the flexural rigidity of the wire.

If the spring is hung up in a vertical position with its upper end rigidly fixed, and a mass  $M$  attached to its lower end so as to be symmetrical about its axis, then, neglecting the mass of the spring, we have

$$F_{x, \phi} = Mg, \quad C_{x, \phi} = 0.$$

Now let the spring be displaced to the configuration ( $x + \delta x, \phi + \delta \phi$ ) and released, then the equations of motion are

$$M \frac{d^2}{dt^2} \delta x = Mg - F_{x+\delta x, \phi+\delta \phi},$$

$$M k^2 \frac{d^2}{dt^2} \delta \phi = -C_{x+\delta x, \phi+\delta \phi},$$

where  $Mk^2$  is the moment of inertia of  $M$  about the axis of the spring; that is,

$$-M \frac{d^2}{dt^2} \delta x = \delta x \frac{d}{dx} F_{x, \phi} + \delta \phi \frac{d}{d\phi} F_{x, \phi},$$

$$-Mk^2 \frac{d^2}{dt^2} \delta \phi = \delta x \frac{d}{dx} C_{x, \phi} + \delta \phi \frac{d}{d\phi} C_{x, \phi};$$

or

$$\begin{aligned} -M \frac{d^2}{dt^2} \delta x &= \delta x \left[ -\frac{B}{l^3} \phi^2 + \frac{B}{l^3} \phi \phi_0 \sqrt{l^2 - x_0^2} \left\{ \frac{1}{\sqrt{l^2 - x^2}} + \frac{x^2}{(l^2 - x^2)^{\frac{3}{2}}} \right\} + \frac{A}{l^3} \phi^2 \right] \\ &\quad + \delta \phi \left[ -\frac{B}{l^3} \{ 2\sqrt{l^2 - x^2} \phi - \sqrt{l^2 - x_0^2} \phi_0 \} \frac{x}{\sqrt{l^2 - x^2}} + \frac{A}{l^3} (2x\phi - x_0\phi_0) \right] \\ -Mk^2 \frac{d^2}{dt^2} \delta \phi &= \delta x \left[ \frac{B}{l^3} \left\{ -2x\phi + x \frac{\sqrt{l^2 - x_0^2}}{\sqrt{l^2 - x^2}} \phi_0 \right\} + \frac{A}{l^3} (2x\phi - x_0\phi_0) \right] \\ &\quad + \delta \phi \left[ \frac{B}{l^3} (l^2 - x^2) + \frac{A}{l^3} x^2 \right]. \end{aligned}$$

If the angles of the unstretched and of the stretched spring are both so small that we can neglect  $\frac{x^2}{l^2}$ , it follows from the

\* Thomson and Tait's 'Natural Philosophy,' vol. i. part ii. p. 141.

equation  $C_{x,\phi}=0$  that we can neglect  $\frac{\phi-\phi_0}{\phi}$ , and then the above equations reduce to

$$\begin{aligned} -M \frac{d^2}{dt^2} \delta x &= \delta x \cdot \frac{A\phi^2}{l^3} + \delta \phi \left[ \frac{(2A-B)x\phi}{l^3} - \frac{Ax_0\phi}{l^3} \right], \\ -Mk^2 \frac{d^2}{dt^2} \delta \phi &= \delta x \left[ \frac{(2A-B)x\phi}{l^3} - \frac{Ax_0\phi}{l^3} \right] + \delta \phi \cdot \frac{B}{l}; \end{aligned}$$

which may be written

$$\left. \begin{aligned} -\frac{d^2}{dt^2} \delta x &= a\delta x + b\delta k\phi, \\ -\frac{d^2}{dt^2} \delta k\phi &= b\delta x + c\delta k\phi, \end{aligned} \right\}$$

where  $a$  and  $c$  are necessarily positive, and  $b$  is small.

The most general form of solution is

$$\delta x = A_1 \sin pt + A_2 \cos pt + B_1 \sin qt + B_2 \cos qt,$$

$$\delta k\phi = \frac{p^2-a}{b}(A_1 \sin pt + A_2 \cos pt) + \frac{q^2-a}{b}(B_1 \sin qt + B_2 \cos qt),$$

where  $p^2$  and  $q^2$  are the roots of the quadratic  $(x-a)(x-c)=b^2$ . We will suppose  $p^2$  to be the greater. The solution may be put into the form

$$\frac{p^2-a}{b} \delta x - \delta k\phi = L_1 \sin (qt + \epsilon_1),$$

$$\frac{q^2-a}{b} \delta x - \delta k\phi = L_2 \sin (pt + \epsilon_2).$$

Thus the motion consists of two normal harmonic vibrations of periods  $\frac{2\pi}{p}$  and  $\frac{2\pi}{q}$ ; in the former  $\frac{p^2-a}{b} \delta x = \delta k\phi$  throughout the motion, and in the latter  $\frac{q^2-a}{b} \delta x = \delta k\phi$ .

It is easily seen that  $p^2-a$  is positive and  $q^2-a$  negative; therefore we conclude that, if  $b$  is a positive quantity, the shorter period of vibration corresponds to a screwing motion similar to the screw of the spring, and the longer to a screwing motion opposite to the screw of the spring, while if  $b$  is negative the reverse is the case.

It is also clear that if  $(c-a)$  is large compared with  $b$  and is  $\left. \begin{array}{l} \text{positive} \\ \text{negative} \end{array} \right\}$ ,  $\frac{p^2-a}{b}$  is  $\left. \begin{array}{l} \text{large} \\ \text{small} \end{array} \right\}$ , and  $\frac{q^2-a}{b}$  is  $\left. \begin{array}{l} \text{small} \\ \text{large} \end{array} \right\}$ ; thus in the  $\left. \begin{array}{l} \text{former} \\ \text{latter} \end{array} \right\}$  case the vibrations of  $\left. \begin{array}{l} \text{shorter} \\ \text{longer} \end{array} \right\}$  period cor-



respond to  $\delta x = 0$ , and those of  $\left. \begin{array}{l} \text{longer} \\ \text{shorter} \end{array} \right\}$  period to  $\delta \phi = 0$ , approximately.

If, however,  $\frac{c \sim a}{b}$  is finite and equal to  $2\lambda$ , we have, when the system is vibrating in one of its normal modes, either

$$(\lambda + \sqrt{\lambda^2 + 1})\delta x = \delta k\phi,$$

or

$$(\lambda - \sqrt{\lambda^2 + 1})\delta x = \delta k\phi$$

throughout the motion, the periods corresponding to these modes being nearly equal. In this case, if the system receives a displacement not represented by either of these equations, the subsequent motion will be compounded of two vibrations, one of which slowly gains upon the other, and will thus exhibit phenomena of intermittence.

For example, if the displacement ( $\delta x = X$ ,  $\delta \phi = 0$ ) be given, this may be resolved into

$$\delta_1 x = X \frac{\sqrt{\lambda^2 + 1} - \lambda}{2\sqrt{\lambda^2 + 1}}, \quad \delta_1 k\phi = X \frac{1}{2\sqrt{\lambda^2 + 1}},$$

and

$$\delta_2 x = X \frac{\sqrt{\lambda^2 + 1} + \lambda}{2\sqrt{\lambda^2 + 1}}, \quad \delta_2 k\phi = -X \frac{1}{2\sqrt{\lambda^2 + 1}};$$

and therefore, when the vibrations of one normal mode have gained half a period on those of the other, the half-amplitude of the  $x$ -vibration will have decreased from  $X$  to  $X \frac{\lambda}{\sqrt{\lambda^2 + 1}}$

and a  $k\phi$ -vibration of half-amplitude  $X \frac{1}{\sqrt{\lambda^2 + 1}}$  will have appeared, while when another half-period is gained the initial conditions will be restored. Thus, while at first the system moves simply with an  $x$ -vibration, this gradually diminishes to a minimum value, and at the same time a  $\phi$ -vibration is gradually set up and grows to a maximum; the latter vibration then decreases and finally vanishes, while the former increases until it reaches its initial value, and then the phenomena recur.

It is easy to see that a similar intermittence will be exhibited if the system is started with a  $\phi$ -vibration only.

The above results may readily be verified experimentally by employing as the mass  $M$  a body of adjustable moment of inertia. The most interesting case is that in which  $k$  is adjusted so that  $\lambda$  is rendered very small, when the energy

is seen to be transferred with almost perfect completeness from  $x$ -vibrations to  $\phi$ -vibrations and back again.

The condition for the vanishing of  $\lambda$  is of course

$$\frac{A\phi^2}{l^3} = \frac{B}{lk^2};$$

or, since to our order of approximation  $l = r\phi$ ,

$$k^2 = \frac{B}{A} r^2.$$

It is also of interest to produce, by means of a series of suitably timed small impulses, the normal modes of vibration of such a system and to demonstrate the permanence of each.

If, however, the object in view is the determination of elastic constants, it is convenient to arrange that  $(c-a)$  shall be large compared with  $b$ . In this case, as we have seen, pure  $x$ -vibrations and pure  $\phi$ -vibrations are practically the two normal modes, and the periodic times of the former and the latter are given by

$$t_1 = \frac{2\pi}{\sqrt{a}} = 2\pi \sqrt{\frac{Mlr^2}{A}},$$

$$t_2 = \frac{2\pi}{\sqrt{c}} = 2\pi \sqrt{\frac{Mlk^2}{B}}.$$

If the mass  $m$  of the spring itself cannot be neglected, we can allow for it, if small compared with  $M$ , by taking  $M + \frac{1}{3}m$  as the vibrating mass, and  $Mk^2 + \frac{1}{3}mr^2$  as its moment of inertia\*.

Let us consider the case of a spring made of circular wire of radius  $\rho$ . If we may assume the material to be homogeneous and isotropic, an assumption which is undoubtedly a weak point of all methods of determining the elastic constants of a material by experiments on wires, we have

$$A = \frac{\pi}{2} n\rho^4, \quad B = \frac{\pi}{4} E\rho^4,$$

where  $E$  and  $n$  are respectively the Young's modulus and the rigidity of the material. From the above we obtain

$$\frac{E}{n} = \frac{2B}{A} = 2 \times \frac{Mk^2 + \frac{1}{3}mr^2}{Mr^2 + \frac{1}{3}mr^2} \cdot \frac{t_1^2}{t_2^2},$$

an equation involving only quantities easy of measurement, and hence Poisson's ratio, which is equal to  $\frac{1}{2}\left(\frac{E}{n} - 2\right)$ , is determined.

\* Lord Rayleigh's 'Theory of Sound,' § 156.

In addition, if the values of  $l$  and  $\rho^4$  are obtained,  $E$  and  $n$  can be separately calculated.

Some observations were taken upon different lengths of one of Salter's steel springs ( $r=1.494$  cm.), using as the vibrating body one whose moment of inertia could be varied by known amounts from an arbitrary value  $K$  by moving two equal masses in and out along a bar.

The following is a specimen of the numbers obtained, in C.G.S. measure :—

*Exp. 1.*— $\phi=300\pi$ ,  $l=1408$ ,  $x=78$ ,  $m=130.5$ ,  $M=267$ .

Moment of Inertia.	$t_1$ .	$t_2$ .
$K + \frac{1}{3}mr^2 + 586$ . . .	1.473	1.888
„ + 1700 . . .	1.477	2.505
„ + 3400 . . .	1.474	3.228
„ + 5680 . . .	1.475	3.986

Whence

$$\frac{B}{4\pi^2 l} = 413, 410, 416; \text{ mean } 413.$$

$$\frac{A}{4\pi^2 l} = 319, 318, 318, 318; \text{ mean } 318.$$

And as a verification we can deduce

$$K + \frac{1}{3}mr^2 = 886, 892, 903, 884; \text{ mean } 891,$$

which gives for  $K$  the value 794.

The results of the experiments are exhibited in the following table :—

$\phi$ .	$l$ .	$M$ .	$m$ .	$A$ .	$B$ .	$K$ .
$300\pi$	1408	267	130.5	$1.77 \times 10^7$	$2.30 \times 10^7$	794
$200\pi$	939	267	87	$1.78 \times 10^7$	$2.29 \times 10^7$	785
$100\pi$	469	267	43.5	$1.77 \times 10^7$	$2.28 \times 10^7$	791
$300\pi$	1408	533	130.5	$1.79 \times 10^7$	$2.28 \times 10^7$	

The last experiment of the above series was made by attaching an additional mass to the vibrating body, so that  $x$  was increased to 125, and of course  $K$  was changed.

Thus we see that the method furnishes consistent results and we deduce for this specimen of steel,

$$\frac{E}{n} = \frac{2B}{A} = 2.57.$$

Also, since for our wire  $\rho$  is about .0617 centim., we obtain as approximate values,

$$E = 2.00 \times 10^{12},$$

$$n = 7.79 \times 10^{11}.$$

An experiment with a spring of hard-drawn copper wire gave

$$\frac{E}{n} = 2.76,$$

with the approximate values

$$E = 1.13 \times 10^{12},$$

$$n = 4.10 \times 10^{11}.$$

**XLV. On the Velocities of the Ions and the Relative Ionization-Power of Solvents.** By W. C. DAMPIER WHETHAM, M.A., Fellow of Trinity College, Cambridge\*.

FROM a knowledge of the electrical conductivity and migration-constant of a solution, Prof. F. Kohlrausch has shown us how to calculate the velocity with which its ions must travel in order that, in accordance with Faraday's law, a given current should be carried (Wied. *Ann.* xxvi.).

Prof. O. Lodge experimentally determined the velocity of the hydrogen ion as it travelled through a jelly solution of sodium chloride and so formed hydrochloric acid, the presence of which was indicated by the decolorization of phenolphthalein. When the ion was driven by a potential gradient of one volt per centimetre the speed came out 0.0029 centimetre per second, a number agreeing in a most remarkable manner with Kohlrausch's theoretical value 0.0030 for a decinormal solution (B.A. Report, 1886).

The author of this paper has observed the specific ionic velocity of other ions, such as copper and the bichromic-acid group ( $\text{Cr}_2\text{O}_7$ ), by tracing the motion of the junction of two salt-solutions (one of which is of different colour from the other) under the influence of an electric current (Trans. Roy. Soc. 1893 A.). The results agree with Kohlrausch's numbers even in the case of alcoholic solutions, the conductivities of which are much less than those of the corresponding aqueous solutions.

Certain substances, *e. g.* ammonia and acetic acid, have been regarded as exceptions to the application of the theory. From a knowledge of the conductivity and migration-constants of acids such as nitric and hydrochloric, we can

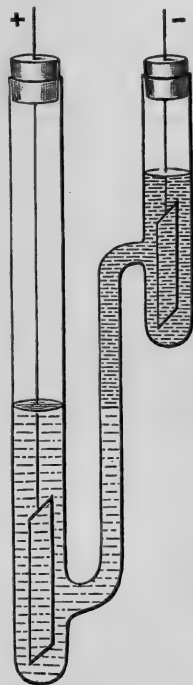
\* Communicated by the Author.

calculate the velocity of the hydrogen ion; and from the same constants for a solution of (say) sodium or potassium acetate, we can get the velocity of the acetic-acid group  $C_2H_3O_2$ . If we calculate what conductivity these velocities would give to a solution of acetic acid (whose ions are  $H$  and  $C_2H_3O_2$ ) of strength 0.1 gram equivalent per litre, we obtain a number greater than the observed result in the ratio of 3168 to 46.

In order to observe whether the velocity of the ions was reduced in the same proportion as the conductivity, the velocity of the hydrogen ion through a solution of sodium acetate was determined by Lodge's method.

The apparatus used is represented in the figure, and was the same as that employed in the earlier investigation above mentioned. Ordinary aqueous solutions were at first set up; but the junction did not travel uniformly, and agar jelly solutions were found to be much better for this purpose. A preliminary investigation was made to examine the influence of the jelly.

The velocity of the bichromic-acid group when driven by a potential gradient of one volt per centimetre was determined by filling the longer limb of the tube with a solution of potassium bichromate in agar jelly just strong enough to set, and the shorter with a similar solution of potassium chloride. A current was then passed across the junction by connecting the electrodes with a battery of storage-cells giving an electromotive force of about 50 volts. The bichromic-acid group travels in a direction opposite to that of the current and displaces the chlorine, so that the colour-boundary moves. If  $v$  represents the observed velocity,  $A$  the area of cross section of the tube at the point of junction of the solutions,  $r$  the specific resistance of the solution, and  $\gamma$  the strength of current as shown by a galvanometer empirically graduated by means of a Daniell's cell and box of resistance-coils, it is easy to prove that the specific ionic velocity of the ion causing the change of colour is



$$v_1 = \frac{vA}{\gamma r},$$

when the potential gradient along the tube is unity. In the case of the  $\text{Cr}_2\text{O}_7$  group travelling through an agar-jelly solution of decinormal strength  $v_1 = \cdot 00044$  centim. per second. In the earlier investigation the same group travelled through an aqueous solution of corresponding strength with a velocity of  $\cdot 00047$  centim. per second. The effect of the jelly is thus to slightly retard the motion, but the alteration appears to be not more than about 10 per cent.

The use of jelly having been thus justified, a solution of sodium acetate (whose strength was afterwards found to be about 0.07 grm. equiv. per litre) in agar jelly was prepared and coloured red with phenolphthalein, just enough caustic soda being added to bring out the full colour. Half of this was decolorized by means of a few drops of dilute acetic acid, and placed in the longer limb of the tube. When it had cooled and become solid, the alkaline red portion was poured into the other limb and also allowed to solidify. A glass scale was fixed behind the junction-tube, and the whole placed in front of a window. The position of the boundary was then read off on the scale by means of a telescope. An electromotive force of about 40 volts was applied, and the velocity with which the boundary between the coloured and colourless solutions travelled observed, readings being taken at intervals of half an hour. The details of the first set of observations are:—

Time. h m	Galvanometer- reading.	Position of boundary.	Velocity in centim. per hour.
11 47	41°0	21.97	
11 48		21.96	
11 49		21.95	
12 17	41°0	21.71	} $\cdot 505$
12 18		21.71	
12 19		21.70	
12 47	41°1	21.51	} $\cdot 40$
12 48		21.51	
12 49		21.50	

Similar sets of observations were then made at intervals of 10 minutes, the following being the space traversed in centimetres during that time:—

$\cdot 10$	$\cdot 09$	$\cdot 09$	$\cdot 09$	$\cdot 09$	$\cdot 09$	$\cdot 08$
$\cdot 09$	$\cdot 09$	$\cdot 09$	$\cdot 09$	$\cdot 09$	$\cdot 08$	$\cdot 08$
$\cdot 07$						

The final mean velocity deduced from these figures, by

allowing weight to each in proportion to the time-interval used in obtaining it, comes out 0.48 centim. per hour, and the mean galvanometer reading  $41^{\circ}0$ .

The specific resistance of the solution was measured by using a Wheatstone's bridge with alternating currents, and gave 246.2 legal ohms per cubic centimetre when reduced to  $18^{\circ}\text{C}$ .

The area of cross section was determined by weighing the water required to fill an observed length of the glass tube, and found to be 0.430 square centim.

The strength of the current was shown by the galvanometer-reading to be  $\frac{1}{278}$  ampere. Substituting these values in our equation, we get for the hydrogen ion travelling through a solution of sodium acetate in agar jelly whose concentration is 0.07 gram equivalent per litre, when urged by a potential gradient of 1 volt per centimetre, a velocity of

**0.000065 centimetre per second.**

The value given by Kohlrausch for the same ion is 0.0030 centim. per second, so that in acetates its speed is reduced in the ratio of 1 to 46.

The ratio of the conductivity of a solution of acetic acid of the strength used above to that of a decinormal solution of hydrochloric acid is 1 to 59.

Thus the velocities of the ions are reduced in about the same proportion as the conductivity, and even in such cases as these the conductivity can be calculated from a knowledge of the opposite ionic velocities. It appears that all the factors determining the conductivity of a solution primarily act by exerting an influence on the ionic velocities. These factors may be (first) the "ionization," *i. e.* the average fractional time during which an ion is on the whole active (in whatever its activity may really consist); and (secondly) the resistance offered by the solution to its motion by reason of viscosity.

It seems probable that the "ionization" power of different solvents is largely dependent on their specific inductive capacities. Prof. J. J. Thomson has pointed out that the effect of immersing a molecule held together by electric forces in a medium of high specific inductive capacity is to greatly reduce the forces between the atoms. In this manner they may acquire the freedom necessary for electrolytic activity, which would, for any one salt, be proportional to the specific inductive capacity of the solvent in which it was dissolved.

If we assume that the resistance of a liquid to the passage of an ion through it depends on its ordinary viscosity, we ought to be able to calculate the relative conductivities of a

salt in different solvents. Some numbers have already been given in the July number of 'Science Progress,' but for the sake of convenience they are reproduced here. The values of the specific inductive capacities of water and ethyl alcohol have been determined by several observers; but apparently the only number for methyl alcohol is one given by Teneschin, so his values for all three liquids are taken, viz. water 83.7, methyl alcohol 32.65, ethyl alcohol 25.8. Correcting these numbers for the viscosities (100; 63; 120) we get the following values, which should, if our assumptions are correct, be proportional to the molecular conductivities of a salt in the three solvents:—

Water = 100; Methyl Alcohol 63; Ethyl Alcohol 26.

Since these are measured for the pure solvent, they should give the relative molecular conductivity of an infinitely dilute solution. An investigation on the conductivities of very dilute solutions of calcium chloride in ethyl and methyl alcohols is now being made by Mr. Fitzpatrick and the present writer. There are not for these cases such definite limiting values as for water solutions, but the following relative numbers (that of the infinitely dilute aqueous solution being taken as 100) correspond to the greatest dilutions reached:—

Water 100; Methyl Alcohol 70; Ethyl Alcohol 23.

The approximation of these numbers to those given above suggest that the specific inductive capacity and the viscosity are at all events the chief factors in determining the "relative ionization power" of a solvent.

Trinity College, Cambridge,  
August 15, 1894.

#### XLVI. *On Dielectrics.* By ROLLO APLEYARD \*.

**M**OST dielectrics, when submitted to the ordinary "insulation" test, show an apparent increase of resistance under the action of the testing-current. That is to say: from the moment the current has been applied, the galvanometer-spot, having reached its maximum position, falls gradually towards zero with time. The rate of this diminution, at any instant, is a measure of the so-called "electrification" of the dielectric at that instant. For commercial purposes the "electrification" is usually computed between the first and second minutes from the moment of charge; the value thus determined is an excellent confirmatory guide

\* Communicated by the Physical Society: read May 11, 1894.



to quality, if the general history of the material and the peculiarities of manufacture are understood. But, apart from its merely commercial bearing, "electrification" presents a wide field for scientific research. The use of the term "electrification" for this rate of change of the apparent resistance of a dielectric with the time of application of the charging current, may be called into question by those who prefer the words "polarization," or "absorption;" but, in the present stage of our knowledge of the action which determines this change, it has been thought better to adopt a term which is never mistaken in practice than to use an ambiguous expression, founded upon an equally uncertain hypothesis. "Electrification" seems to be the net result of many simultaneous actions, some of which are very obscure; the physical mechanism implied in the process is subtle and mysterious, the experimental observations are difficult to reconcile among themselves, and there is no theory to adequately account for the phenomena. It is not proposed, here, to make any attempt at solving the difficulties, but rather to present them in the form of experimental results.

### *Celluloid.*

The first substance to be dealt with, in this regard, is "celluloid." As far as can be judged by inspection it appears to be a compound of guncotton and camphor, with a trace of lime—possibly in the form of sulphate. When seen through the microscope, small white spots become visible in a translucent yellowish substance. In texture "celluloid" resembles "cordite," but it is of lighter colour, inflammable but not explosive. The insulation of this substance was, at first, measured in the following way:—A thin circular sheet of celluloid was placed between two plane surfaces of brass 11 inches in diameter. A margin of celluloid was allowed, to prevent leakage over the edges; and a heavy weight was put upon the top plate. When this sheet was submitted to the action of a current, there was no such apparent increase of resistance as is usually to be observed with dielectrics. The galvanometer, in fact, indicated the reverse effect—the deflexion gradually increasing with time. No actual fault could be detected in any of the samples, and yet the "electrification" was negative. This curious effect was the more to be noticed as the voltage of the testing-battery was increased. The actual insulation resistance, calculated for the same sample, with this apparatus, under various currents, showed that the resistance changed enormously with the testing voltage.

In this case, and in all experiments here mentioned, the

insulation has been computed from the deflexions obtained after the corresponding voltage had been applied for one minute. The upper readings correspond with increasing voltages; the lower curve completes the cycle with diminishing voltages, and shows the falling-off of insulation with current, in a manner curiously like the hysteresis curve of iron. The observed values are given in Table I.

TABLE I.—Celluloid Sheet.

		volts 150	volts 300	volts 600	volts 750	volts 600	volts 300	volts 150
Galvanometer Readings.	1 <sup>m</sup> ...	19.8	85.8	533	1310	605	152	45
	2 <sup>m</sup> ...	20	89.3	554	1338	663	158	45
Corresponding Resistance in megohms. } =		4040	1840	597	303	526	1039	1778

This table includes the actual galvanometer-deflexions from which the insulation-resistance at each voltage was calculated. First and second minute readings are recorded, and exhibit very strikingly the apparently *negative* "electrification,"—the first-minute readings being less than the second-minute readings.

A series of tests was made upon celluloid sheets pressed, in the above manner, between two plane surfaces of metal, and the same general features were observed in each case. As no definite fault could be discovered in any sample, I was led to suppose that the abnormal change in resistance, and the corresponding negative "electrification," were to be accounted for by some complex molecular rearrangement within the substance of the celluloid itself. Leakage over the edges might obviously be urged in explanation, but the conditions did not seem to allow of any serious loss in this manner. While employing unyielding metallic surfaces against the comparatively hard surface of the celluloid, the chances of uneven pressure upon the sheet were very great: which would imply uneven electrical contact between the dielectric and the plates.

The next experiments were made with a view to test the celluloid in perfect contact with the opposed plates; to remove all chances of leakage-error; and to provide, at the same time, a more evenly distributed pressure over the surface. The hard metallic plates were therefore replaced by mercury surfaces

which conformed precisely, and without undue pressure, to the sheet of dielectric ; and, at the same time, made perfect contact with it, leaving no air-spaces or spark-gaps where ozone or other gases might collect.

Circular sheets of celluloid,  $11\frac{1}{2}$  inches in diameter, were employed for these tests. To prevent leakage, a 3-inch margin was allowed all round, so that the working-surface in contact with mercury was  $5\frac{1}{2}$  inches in diameter. The method of fixing the dielectric sheet was as follows :—Two flat ebonite rings,  $5\frac{1}{2}$  inches internal diameter, and  $6\frac{1}{2}$  inches outside, were faced on each side with india-rubber, forming insulating washers. These rings were placed exactly opposite each other, flatwise, one on each side of the sheet to be tested. Circular plates of iron were now laid against the outer faces of the rings, and combined to make two mercury-tight hollow boxes, one on each side of the dielectric. The whole was then gripped vertically in an ebonite vice ; after which mercury was poured in to fill the boxes. This apparatus, with the exception of the insulating rings, is the same as that designed, I believe, by Mr. Evers. The great advantage of the method is that the mercury conforms to the surface of the dielectric, leaving no air-spaces and necessitating no artificial pressure. The surface-leakage can be made as small as desired, by the simple device of leaving enough margin. Experiments made upon dielectrics fixed in this apparatus give results entirely different from those obtained with rigid metallic plates.

A sheet of celluloid  $\cdot 071$  inch in thickness was the first that came under trial. Its behaviour during a cycle of voltage from 150 to 1200 volts is represented in Table II.

TABLE II.

Volts <i>increasing</i> .		Volts <i>diminishing</i> .	
Volts.	Resistance in megohms.	Volts.	Resistance in megohms.
150	82·7	1050	80·7
300	82·3	900	81·0
450	82·0	750	81·3
600	81·5	600	81·5
750	81·2	450	82·0
900	80·8	300	82·3
1050	80·6	150	82·7
1200	80·6		

The curves practically overlap. The insulation falls somewhat with the increase of voltage, but recovers its original value as the cycle is completed. There was no observable "electrification"; the first and second minute readings were in each case identical.

The next sheet of celluloid tested was 6 mils in thickness. Here again there was no sign of "electrification," though there was a distinct diminution of insulation with voltage. This sheet broke down at 1200 volts; there is nothing in the curve to indicate that such a rupture was about to take place. These results are given in Table III.

TABLE III.

<i>Volts increasing.</i>	Resistance in megohms.
150	30.0
300	29.6
450	29.2
600	28.4
750	27.7
900	26.8
1050	26.0
1200	Broke down.

A third sheet, cut from the same specimen as the last, was then tested through a cycle from 150 to 1050 volts; it showed practically no hysteresis and no "electrification," the return values being simply reproductions of the rising ones. There is the same drop in insulation with voltage as in the previous tests, as shown by Table IV.

TABLE IV.

<i>Volts increasing.</i>		<i>Volts diminishing.</i>	
Volts.	Resistance in megohms.	Volts.	Resistance in megohms.
150	26.34	900	22.72
300	25.56	750	23.48
450	24.93	600	24.15
600	24.15	450	24.93
750	23.51	300	25.68
900	22.72	150	26.52
1050	21.89		

The same sheet was then tested between hard metallic plates, the results are indicated in Table IV. A.

TABLE IV. A.

	volts 150	volts 300	volts 450	volts 600	volts 750	volts 900	volts 1050	volts 900	volts 750	volts 600	volts 450	volts 300	volts 150
1 <sup>m</sup>	6	23.5	61.5	161	278	156	158	186	127	117.0	95.0	39.5	11.5
2 <sup>m</sup>	.....	23.7	64.0	171	296	162	162	189	129	118.5	96.5	39.5	.....
	megohms 20,550	10440	6047	3076	870	283	135	199	549	1641	3915	6212	10720

*“Dielectric Hysteresis.”*

“Dielectric hysteresis” is here alluded to in a sense which needs a little explanation. The similarity in shape and character between some of these curves and the well-known forms of the hysteresis curves of magnetism is all that I wish to imply,—it is *not* the phenomenon of “dielectric hysteresis” proper. In an article in the *Electrotechnische Zeitschrift*, 29th April, 1892, p. 227, Steinmetz traces the analogy between a dielectric medium in an electrostatic field and magnetic bodies in a magnetic field, with a view to determining whether the loss of energy in dielectrics, under the influence of an alternating electrostatic field, would follow a law similar to that which defines the magnetic losses due to magnetic hysteresis. The experiments of Steinmetz, and of Arno, have gone to show that the energy expended in a dielectric medium, in an electrostatic field of alternating potential, is sensibly proportional to the square-root of the intensity of the electrostatic field. These losses are due to “dielectric hysteresis” proper, and are quite distinct from the mere change of resistance with voltage here described. The experimental results of Steinmetz should, however, be corrected for this other phenomenon of change, which, for the time being, we may call “dielectric mutability,” or any other term which denotes the variation of resistance with voltage; for it is clear that the energy expended during a cycle of potential cannot rightly be calculated upon the basis of constant resistance assumed by Steinmetz. With this correction, if it could be determined and applied to his results, the observed values, notwithstanding their present close agreement with those calculated, may possibly be brought even nearer to conformity.

*"Residual Charge."*

The residual charge becomes a very small quantity a few minutes after breaking circuit; consecutive voltages can therefore be applied without having to wait very long for the practical disappearance of the last charge. In the above tests it was made a rule never to send a current into a sheet until the previous charge had vanished to within  $\frac{1}{2}$  per cent. Although, under these conditions, the charge is quickly got rid of, yet during the first few seconds the amount left in may be very considerable. Conversely, the celluloid takes up its charge comparatively tardily. If, for instance, an attempt is made to determine the capacity of the sheet, when in the mercury apparatus, by the simple discharge method, an eye which is accustomed to watching the "throw" of the galvanometer will at once observe that the needle is under the action of an extended discharge and not of a sudden impulse. When first this phenomenon was observed I carried out the following experiment:—The celluloid was charged from 20 cells for 15 seconds. It was then discharged, not through the galvanometer, but through the short-circuit key. After two seconds the short-circuit key was opened, and there was a discharge of a few degrees to the right—that is, in the "discharge" direction; this fell in a few seconds across the zero to 5 divs. on the left, where it remained perfectly steady. This curious reversal of sign was at first rather puzzling; if the spot had merely fallen to zero, it would have been easy to refer it to complete loss of charge; if it had fallen a little to the right of zero, it could have been attributed to incomplete loss of charge; but falling, as it did, on the negative side of zero, a novel case was presented.

After several repetitions, charging with various potentials up to as high as 900 volts, this reversal still manifested itself, although the time required to attain it was of course greater as the testing-voltage increased. Days and nights of short-circuiting would not wipe it out; whatever was tried, it remained always the same negative deflexion. It is, in fact, an initial permanent E.M.F. of about .0006 of a volt with which nothing seems to interfere. It is apparently due to the contact of the mercury with the celluloid; it did not appear when metallic plates were used. This point having been so far settled, the experiments on slow discharge were repeated with 100, 200, 400, and 600 cells; the corresponding discharge-readings—after short-circuiting the sheet for two seconds in each case before discharge—were respectively 18, 36, 57, and 80 divs., falling to zero, or very nearly to zero in a few minutes, and ultimately crossing the zero to -5. The discharge from a standard microfarad charged to 30 volts is

11,103 scale-divs. The instantaneous discharge from the celluloid sheet ( $5\frac{1}{2}$  in. diam., .00615 inch thick) with the same voltage, was 115 divs., which is the mean of the two readings obtained by reversing the battery. The test can scarcely be regarded as a capacity test under the above conditions. It is recorded here simply to show the phenomenon of slow discharge, and the existence of the permanent initial E.M.F.

*Gutta-Percha.*

Appended are the results of some tests upon a sheet of pure gutta-percha, in the mercury apparatus, at high voltages. The thickness of this sheet was about 2 mils; the diameter of the circular mercury surface in contact with it, bounded by the insulating rings, was, as before,  $5\frac{1}{2}$  inches. Curves drawn from the tabulated results exhibit the phenomenon of dielectric hysteresis, and show that the effect of the current, up to a certain point, is to increase the resistance; there is a subsequent tendency in the opposite direction, which would probably end in the breaking-down of the sample. There was no initial electromotive force to be observed with the gutta-percha.

Four separate tests were made upon the sheet, two with a cycle commencing at maximum volts, and two commencing at the minimum. In each case, whether beginning at the maximum or minimum volts, there was a decided increase of resistance as the result of a cycle. With such a thin sheet as 2 mils the test was a very severe one for the gutta-percha; hence it is not surprising that the curves are somewhat broken. Two-thousandths of an inch of material is here effectively contending against 1200 volts, and setting up a barrier of 3000 million ohms over an area of  $5\frac{1}{2}$  inches.

A very interesting point about these four tests is that when the cycle commences at maximum voltage the subsequent readings are far steadier, and the curve of resistance and voltage smoother, than when minimum volts are started with; this is clearly indicated by a comparison of the four curves which may be drawn from these tables.

There is no absolute need to short-circuit the apparatus in order to remove the residual charge of the sheet; but short-circuiting probably quickens the process. This is a matter for further experiment. It was found that the sample of gutta-percha completely lost its charge after twenty-four hours, whether short-circuited or not, and during that time it regained its normal condition as regards insulation resistance. Twenty-four hours was therefore allowed between each of the four tests upon the gutta-percha sheet. As a rule, about ten minutes' rest was given between the consecutive voltages of individual tests; this was found to be time enough to practically discharge the sheet when short-circuited.

TABLE V.—Gutta-Percha sheet ( $G_2$ ).  
(Volts *increasing*.)

	volts 150	volts 300	volts 450	volts 600	volts 750	volts 900	volts 1050	volts 1200
1 <sup>m</sup> ...	26.2	49.8	68.4	82	unsteady 130	unsteady 150	unsteady 160	steadier 171
2 <sup>m</sup> ...	25.6	47.6	65.0	unsteady 98	117	135	160	159
	2272 <sup>~</sup>	2384 <sup>~</sup>	2614 <sup>~</sup>	2910 <sup>~</sup>	2290 <sup>~</sup>	2383 <sup>~</sup>	2602 <sup>~</sup>	2789 <sup>~</sup>

	volts 1050	volts 900	volts 750	volts 600	volts 450	volts 300	volts 150	volts 1200
1 <sup>m</sup> ...	steady 126	100	73	53.5	38.5	24.5	12.0	170
2 <sup>m</sup> ...	126	100	75	49.0	31.0	18.0	9.2	148
	3303 <sup>~</sup>	3572 <sup>~</sup>	4079 <sup>~</sup>	4459 <sup>~</sup>	4645 <sup>~</sup>	4845 <sup>~</sup>	4961 <sup>~</sup>	2805 <sup>~</sup>

Temp. = 66° F.

TABLE VI.—Gutta-Percha sheet ( $G_2$ ).  
(Volts *diminishing*.)

	volts 1200	volts 1050	volts 900	volts 750	volts 600	volts 450	volts 300	volts 150
1 <sup>m</sup> ...	steady 171.2	137.3	112.5	91.8	71.8	54.2	39	20.0
2 <sup>m</sup> ...	166.0	135.0	111.5	89.5	68.0	49.0	34	17.7
	3220 <sup>~</sup>	3510 <sup>~</sup>	3670 <sup>~</sup>	3760 <sup>~</sup>	3840 <sup>~</sup>	3320 <sup>~</sup>	3530 <sup>~</sup>	3470 <sup>~</sup>

	volts 300	volts 450	volts 600	volts 750	volts 900	volts 1050	volts 1200
1 <sup>m</sup> ...	38.5	53.5	69.5	84	100	118.5	steady 145
2 <sup>m</sup> ...	33.8	48.0	64.5	81	98	a little unsteady 119.0	143
	3570 <sup>~</sup>	3870 <sup>~</sup>	3970 <sup>~</sup>	4130 <sup>~</sup>	4130 <sup>~</sup>	4070 <sup>~</sup>	3900 <sup>~</sup>

23rd April, 1894.

Temp. = 64°·5 F.



TABLE VII.—Gutta-Percha sheet ( $G_2$ ).  
(Volts *increasing*.)

	volts 150	volts 300	volts 450	volts 600	volts 750	volts 900	volts 1050
1 <sup>m</sup> ...	22.0	unsteady 74	unsteady 85	steady 84.5	steady 100.0	unsteady 118.2	unsteady 143
2 <sup>m</sup> ...	21.6	54	71	80.5	94.5	118.0	139
	2960~	1730~	2280~	3050~	3230~	3260~	3140~

	volts 1200	volts 1050	volts 900	volts 750	volts 600	volts 450	volts 300	volts 150
1 <sup>m</sup> ...	unsteady 167	154	125	96.5	70.5	52.5	34.0	16.6
2 <sup>m</sup> ...	193	152	123	96.0	67.0	44.2	27.5	14.6
	3070~	2920~	3080~	3350~	3660~	3690~	3760~	3920~

24th April, 1894.

Temp. = 63° F.

TABLE VIII.—Gutta-Percha sheet ( $G_2$ ).  
(Volts *diminishing*.)

	volts 1200	volts 1050	volts 900	volts 750	volts 600	volts 450	volts 300	volts 150
1 <sup>m</sup> ...	231	143	99	68	50.0	37.6	25.8	13.0
2 <sup>m</sup> ...	187	131	94	65	48.7	35.6	24.0	12.3
	1620~	2290~	2830~	3430~	3720~	3700~	3570~	3550~

	volts 300	volts 450	volts 600	volts 750	volts 900	volts 1050	volts 1200
1 <sup>m</sup> ...	25.6	37.4	47.0	58	73	91	109
2 <sup>m</sup> ...	23.8	34.6	44.5	58	75	92	117
	3600~	3720~	3970~	4020~	3780~	3600~	3430~

25th April, 1894.

Temp. = 62° F.

The small opaque white spots, observed within the celluloid under the microscope, led to some further experiments to investigate the effect of isolated foreign particles within the substance and upon the surface of dielectrics. Coarse brass filings were scattered as thickly as possible over one face of a warmed strip of gutta-percha, 16 inches long, 2 inches wide, and  $\frac{1}{4}$  inch thick. The insulation of such a strip is not exactly what might be expected; when tested even with 750 volts its resistance was practically infinite, and was certainly greater than 600,000 megohms. A charged gold-leaf electroscope could not be discharged with such a strip in this condition. If, however, a wet cloth was passed once over the non-metallic face of the strip, or if it was simply breathed upon, the insulation fell to 5000 megohms, and the strip now easily discharged the electroscope. A round rod of gutta-percha can be warmed and rolled in a heap of brass filings so as to appear almost like a brass rod, and such a rod does not discharge the electroscope. This would be an instructive experiment for schools and instrument-makers.

#### *"Sensitive" Dielectrics.*

The next experiments were made with rods formed of a mixture of gutta-percha and brass filings melted together in various proportions. The length of these rods was about 20 inches, and their diameter  $\frac{3}{4}$  of an inch. Contact was made with the ends for about  $1\frac{1}{2}$  inches by tin-foil which was bound round with wire. It is found that, for small proportions of brass filings, the resistance between the ends of these rods is exceedingly high, and this high resistance is maintained until about 2 parts, by weight, of brass are mixed with one part, by weight, of gutta-percha. Here a "critical" point of proportionality between the two substances occurs, *under* which the rods have a very low resistance, of something like one ohm; and *above* which the resistance is exceedingly high, and can only be measured in megohms. Several rods were made at or near this "critical" point, and in no case could a medium resistance of, say, a few hundred ohms be attained. All the rods were either of very high or very low resistance.

The method of making them is to warm a sheet of gutta-percha upon a hot plate, using French chalk to prevent sticking. The filings are sprinkled in as soon as the sheet becomes soft. The whole is then made up into a pudding, which is again flattened out into a sheet; this is repeated until a good mixture is arrived at. The compound is then rolled into rods.

TABLE IX.

No. of Rod.	Proportion by weight $\frac{\text{G.P.}}{\text{Brass}}$	Approximate Resistance.
1 .....	$\frac{1}{2}$	·2 ohm.
2 .....	?	·07 „
3 .....	$\frac{1}{3}$	·11 „
4 .....	$\frac{1}{1}$	$\infty$ .
5 .....	$\frac{2}{1}$	$\infty$ .
6 .. .....	$\frac{2}{3}$	283,000 megohms.
7 .....	$\frac{4}{7}$	173,000 „
8 .....	$\frac{1}{2}$	$\infty$ .
9 .....	$\frac{1}{2}$	770 megohms.
10 .....	$\frac{1}{3}$	·37 ohm.
11 .....	$\frac{2}{5}$	1·68 „
12 .....	$\frac{1}{2}$	19 ohms.
13 .....	$\frac{4}{9}$	3·9 „
14 .....	$\frac{4}{11}$	·48 ohm.
15 .....	....	1·5 megohm.

Table IX. gives the proportion by weight of these rods and the corresponding resistance. When rods made up in this way are submitted to the action of oscillating discharges, they behave in a similar manner to the "impulsion" cells of Prof. Minchin and the tubes of M. Branly. If, for instance, one of the low-resistance rods of, say, four parts by weight of gutta-percha to nine of brass filings is connected to one arm of a Wheatstone's bridge and balanced, an oscillatory discharge made anywhere near it will, in nearly all cases, produce a considerable diminution of resistance—in some cases amounting to more than 10 per cent., and, in one experiment, to as much as 45 per cent. This charge remains until restored to the former condition of things by a slight mechanical tap. I have repeated this experiment upon seven different rods, and have, in each case, obtained a diminution when the discharge-spark passed at the oscillator. The small-resistance

rods of Table IX. were all sensitive to these electromagnetic oscillations. The high-resistance rods do not come within the range of measurement of the usual form of Wheatstone's bridge; the ordinary insulation-test was therefore applied, using a battery of 400 Leclanché cells. In this way resistances up to 600,000 megohms could be measured. A rod composed of 4 parts, by weight, of gutta-percha, to 7 parts of brass filings had practically infinite resistance. Another, having 2 parts, by weight, of gutta-percha to 3 of brass, had 100,000 megohms. A third, made up in the ratio of 4 parts gutta-percha to 7 of brass, was of infinite resistance. Four rods were made in the proportion 1 gutta-percha to 2 of brass, which is near the critical ratio of conductor to insulator; their resistances were, respectively,  $\infty$ , 40 megohms, and 12 ohms. The 17 ohm rod exhibited a decided, but not very great diminution of resistance under the influence of the oscillator. Apparently, the high-resistance rods are unaffected by the discharges. The 40 megohm rod was not of very constant resistance, the spot moved up and down the scale; the spark had therefore to be passed at moments when the spot halted,—the result was not very satisfactory. At one time it was thought actually to *increase* the resistance of this rod. The 12 ohm rod was especially interesting from its extreme sensitiveness; in one condition it had a resistance of 19 ohms, the sudden passage of a spark at the oscillator reduced this by 45 per cent. The rod was generally unstable. The 40 megohm rod seemed the one most nearly corresponding, in its galvanometer-readings, with a faulty cable; the readings being erratic. Its resistance has, at times, been as high as 770 megohms. This rod is probably unstable in some opposite direction to the 12 ohm rod; they were both made in the same proportions and in the same manner. In Table IX. they appear as No. 9 and No. 12 respectively.

#### *Alternating Voltages.*

Tests were now made upon specimens submitted to alternating currents, and I have to thank Mr. George Bousfield for assisting me in this part of the experiments. I took the strip sprinkled with filings, and two rods; these were first tested for insulation in the ordinary way, with the following results:—

Dielectric.	Resistance.
Strip =	$\infty$ .
No. 6 =	283,000 megohms.
No. 9 =	47.2 megohms.

The strip began to break down under the action of the alternating current at 900 volts ; at 3000 volts it was emitting small local arcs, some crimson, others violet. After the application for some time of this high voltage the number and brilliancy of the arcs diminished,—the insulation had apparently improved. At 5500 volts there were bright discharges similar to the first. These were not of the nature of long sparks, but of small local arcs.

Rod No. 6 gave way at 6500 volts and exhibited the same apparent improvement in insulation. The arcs shot out in miniature flames, like very small blowpipe blasts ; locally, as in the case of the strip.

With rod No. 9 sparking commenced at 1500 volts, having the appearance of small beads of crimson and violet light burning themselves out at fixed points. When these specimens had become cool their insulation was again tested.

Dielectric.

Resistance.

Strip =  $\infty$ .

No. 6 = 70,750 megohms.

No. 9 = 2020 megohms.

The strip thus appears to have recovered entirely. No. 6 has fallen to a quarter of its first value, and No. 9 has greatly improved, under this trying ordeal.

Rod No. 15 was compounded of iron filings, Sr, &c., with a view to obtaining a brilliant discharge. The salts brought the insulation down rather low ; there was a great deal of heat generated, and little else. Such a rod should probably be made simply of metallic powders intermixed with the dielectric.

**XLVII.** *On the Resistance of a Fluid to a Plane kept moving uniformly in a direction inclined to it at a small angle.* By Lord KELVIN\*.

§ 1. **L**ET  $q$  be the velocity ;  $i$  its inclination to the plane ; and  $u, v$  its components in and perpendicular to the plane. We have

$$u = q \cos i, \quad v = q \sin i.$$

§ 2. Suppose now the moving body to be not an ideal infinitely thin plane, but a disk of finite thickness very small in comparison with its least diameter, and having its edges everywhere smoothly rounded. If the fluid is inviscid and incompressible, and the boundary containing it perfectly

\* Communicated by the Author.

unyielding, the motion produced in the fluid from rest, by any motion given to the disk, is determinately the unique motion of which the energy is less than that of any other motion possible to the fluid with the given motion of the disk. We suppose the disk to be *very* thin, and therefore the profile-curvature at every point of its edge to be *very* great: there is no limit to the thinness at which the proposition could cease to be true; so it still holds in the ideal case of an infinitely thin disk, when the fluid and its boundary fulfil the ideal conditions of the enunciation.

§ 3. But in nature every fluid has some degree of viscous resistance to change of shape; and any viscosity however small (even with ideally perfect incompressibility of the fluid and unyieldingness of the boundary) would prevent the infinitely great velocities at the edge of the disk which the unique minimum-energy solution gives when the disk is infinitely thin; and would originate so great a disturbance in the motion of the fluid that the resistance to the motion of the disk would probably be very nearly the same whatever the actual value of the viscosity, if not too great in comparison with the velocity of the disk multiplied by the least radius of curvature of the boundary of its area. No approach, however, has hitherto been made towards a complete mathematical solution of any case of this problem, or indeed of the motion of a body of any shape through a viscous fluid, except when, as in Stokes's original solutions for the globe and circular cylinder, the motion is so slow that its configuration is the same as it would be if it were infinitely slow, and when therefore\* the velocity of the fluid at every point is equal to, and in the same direction as, the infinitesimal static displacement of an elastic solid when a rigid body imbedded in it is held in a position infinitesimally displaced from its position of equilibrium, in the manner translationally and rotationally corresponding to the translational and rotational velocity given to the rigid body in the fluid.

§ 4. It has occurred to me, guided by the teaching of William Froude regarding the continued communication of momentum to a fluid by the application of force to keep a solid moving with uniform translational velocity through it, that an approximate determination of the resistance, which is the subject of the present communication, may probably be

\* The equations for the *steady* infinitely slow motion of a viscous fluid are identical with those for the equilibrium of an elastic solid. See 'Mathematical and Physical Papers' (Sir W. Thomson), vol. iii., art. cxix. §§ 17. 18.

found by the following method, with result expressed in § 9, which I venture to give as a *guess*, and not as a satisfactory mathematical investigation.

§ 5. Considering a disk of finite thickness, however small, moving in an inviscid incompressible liquid within an unyielding boundary, and, for a moment, thinking only of the  $u$ -component of the motion, according to the notation of § 1, let  $E$  and  $E'$  denote the front and the rear parts of the edge, respectively. Imagine now instead of the real motion of the unvarying solid disk through the fluid, that the disk grows all over  $E$ , by rigidification and accretion of the fluid in front of it, and melts away from  $E'$  by liquefaction of the solid. In an infinitesimal time  $\delta t$ , the extent of the accretion in front of  $E$  will be  $u\delta t$ . Now if the  $v$ -component of the motion of the disk is maintained without diminution during this accretion, a force,  $F$ , equal to  $(I' - I)/\delta t$ , must be applied from without, perpendicular to the disk;  $I$  denoting the impulsive force which would be required to give the  $v$ -component velocity to the unaugmented disk, and  $I'$  that required to give the same velocity to the augmented disk. The point of application of the force  $(I' - I)/\delta t$  must be that of the resultant of impulses  $I'$  and  $-I$ , applied at the hydraulic centres of inertia\* of the augmented disk and the unaugmented disk respectively.

§ 6. Sudden cessation of the rigidity by liquefaction of any portion, (finite or infinitely small) of matter of the disk at  $E'$  requires no instantaneous application of force, to prevent change of the  $v$ -motion of the residual solid. The continued gradual liquefaction which we are supposing performed, leaves a Helmholtz "vortex sheet" of finite slip growing out in the liquid, behind  $E'$ , the evolutions and contortions of which are not easily followed in imagination. This sheet is in the form of a pocket of which the lip remains always attached to the solid disk. The space enclosed between it and the disk is filled by the liquid which was solid. It grows always longer and longer by gain of liquid from the melting solid at  $E'$  in front of it, and probably also by its rear extending farther and farther, far away in the wake of the disk.

§ 7. Suppose now that, after having been performed during a certain time  $T$ , the ideal processes of §§ 5, 6 are discontinued, and the resulting solid disk, equal and similar to the original disk, but carried in the  $u$ -direction through a space

\* I call the "hydraulic centre of inertia" of a massless rigid disk immersed in liquid the point at which it must be struck perpendicularly by an impulse, to give it a simple translational motion.

equal to  $uT$ , is left with simply its  $v$ -motion through the fluid maintained. The pocket of liquefied solid will be left farther and farther behind the disk. Its mouth, still always stopped by the solid, will shrink from its original area which was the whole of  $E'$ ; and will become always smaller and smaller, but not infinitely small in any finite time. The neck of the pocket in the wake of the disk will become narrower and narrower, and the whole pocket will be drawn out longer and longer behind; but, through all time, the fluid which was solid will remain separated by a surface of finite slip, or Helmholtz "vortex sheet," from the surrounding fluid, except over the ever diminishing area of the disk, which stops the mouth of the pocket. The motion of the fluid is irrotational outside the pocket, and rotational within it. To keep the solid disk moving with its  $v$ -motion constant, and with no other motion whether rotational or translational, it is necessary to apply force to it. But this force becomes less and less, and approximates to zero, as the vortex-trail becomes finer and finer; and the motion of the fluid in the neighbourhood of the disk approximates more and more nearly to perfect agreement with the unique irrotational motion due to  $v$ -motion of the solid through the fluid.

§ 8. So far we have, in §§ 5, 6, 7, been on sure ground, and every statement is rigorously true, not only for a "disk" of any shape of boundary and of any thickness however small, but also for a solid of any shape, dealt with according to § 5, provided only that the fluid is inviscid and incompressible, and its boundary unyielding. My hypothesis, or "guess" (§ 4), which forms the subject of the present paper, is that default from infinitely perfect fulfilment of all these three conditions would, for an infinitely thin disk kept moving with uniform translational motion ( $u, v$ , § 1), require the continued application to it of force determined in magnitude and position by § 5; *provided  $v$  be very small in comparison with  $u$ .*

§ 9. The result is worked out with great ease for the case of a rectangular disk of which the length,  $l$ , is very great in comparison with the breadth,  $a$ . For this case, by the well-known hydrokinetics of an ellipsoid or elliptic cylinder moving translationally in an inviscid incompressible fluid of unit density, we have

$$I = \frac{1}{4}\pi a^2 l v;$$

and, still using the notation of § 5,

$$I' = \frac{1}{4}\pi (a + u\delta t)^2 l v.$$

Hence

$$F = \frac{1}{2}\pi a l u v;$$



and the distance of the point of application of this force from the middle line of the rectangle is

$$\frac{1}{4}a.$$

Comparison of this hypothetical result, with observation, in respect both to the magnitude of the force and its point of application, will, I hope, form the subject of a future communication.

Eastern Telegraph Company's Cable-ship 'Elcetra,'  
Athens to Genoa, Sept. 3 ... 6, 1894.

XLVIII. "*Densities in the Earth's Crust.*"

By Rev. J. J. BLAKE, M.A., F.G.S.\*

MR. OSMUND FISHER having been unfortunately called upon to categorically assent to or answer my criticisms of a portion of his work on the 'Physics of the Earth's Crust,' has attempted the latter alternative in the April number of this magazine. I had hoped that he would have adopted the former on more careful consideration of the subject; but, as it is not so, I hope I may be excused if I point out still more clearly the gist of my objections to his method.

In several places Mr. Fisher does not seem to recognize that it is not his conclusions but his mathematics that are discussed, for if the mathematics are wrong there are no conclusions to discuss. Thus he begins by stating that if I had more fully mastered his "results," I should not have stated that "the argument ... seems to depend on the greater density of the superficial layer in continental than in oceanic areas," which he observes is the exact opposite of his "conclusion;" but, as ocean water is certainly of less density than rock, this is not a conclusion at all, but a datum—the mathematical problem being this:—Given that the attraction of a sphere on a particle at any point on its surface is constant for all such points— but that the superficial layer in one part is less dense than in another—find the relations between the densities and thicknesses of the underlying layers.

Again, he says it would be absurd to assume any other law of attraction than the Newtonian for the case of nature,—very likely; but the objection is that, if the method were correct, the same results might be deduced even from an absurd law. It is for this reason that I call the functions he speaks of ( $f(\theta)$  &c.) "unknown."

Again, he answers my objection that in his solution "it is

\* Communicated by the Author.

necessary to assume the equality of the two sides to the same degree of approximation as there are layers in the crust," by saying that there is no necessity for such an equality in nature. Just so—that is my objection—that the equality has to be assumed for the sake of the mathematics.

These minor objections, however, and their replies are of comparatively little consequence; and I merely mentioned them as slight indications that should have shown that something was amiss. The main statement, which Mr. Fisher simply repeats, is to the following effect:—If

$$(\sum_m(\tau t) - \sum_n(\tau' t'))f(\theta) + (\sum_m(\tau t^2) - \sum_n(\tau' t'^2))\frac{\phi(\theta)}{a} + \&c. = 0 \quad (A)$$

for any number of assumed values of  $\theta$ , then must

$$\left. \begin{aligned} \sum_m(\tau t) &= \sum_n(\tau' t') \\ \sum_m(\tau t^2) &= \sum_n(\tau' t'^2) \\ \&c. &= \&c. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (B)$$

the  $\tau$ 's denoting densities and the  $t$ 's thicknesses.

That is his fundamental proposition, and what I say is this:—that equations (B) do *not* follow from (A), and that if they were true, they would be of no value.

Even the converse proposition, that if equations (B) are satisfied the series (A) is zero, is only true if the series is convergent; but to deduce (B) from the series (A) being zero it is necessary to show, first, that it is convergent; secondly, that none of the functions  $f(\theta)$ ,  $\phi(\theta)$ , &c., are zero for all values of  $\theta$ , and particularly that it is possible to make  $\phi(\theta)$ ,  $\psi(\theta)$ , &c. zero without making  $f(\theta)$  zero at the same time. This is what I mean by "independent." Mr. Fisher replies to this, that they are not independent, which is exactly my objection, because he has to assume them, *in his work*, to be so. As a matter of fact,

if we take Mr. Fisher's values of  $f(\theta)$ ,  $\phi(\theta)$ ,  $\psi(\theta)$ , as correct, each is a linear function of the other two and all vanish together for the same value of  $\theta$ , so that the coefficient of any one may be distributed amongst the others. Moreover, the only

value of  $\theta$  which makes them zero is given by  $\sin \frac{\theta}{2} = -1$ , which is an impossible value in the problem dealt with, while the occurrence of  $\sin \frac{\theta}{2}$  in the denominator of  $\phi(\theta)$

and  $\psi(\theta)$  shows that the series may well be divergent for small values of  $\theta$ , and, indeed, cannot be a true expression for the attraction when  $\theta=0$ . The true expression is in fact a function of two independent variables  $t$  and  $\sin \frac{\theta}{2}$ ; and if we

attempt to expand it in powers of these the coefficients are found to be indeterminate.

But supposing equations (B) were true, what do they mean?

As  $\tau \tau'$  &c. may be positive or negative, we can write them

$$\tau_1 t_1 + \tau_2 t_2 + \tau_3 t_3 + \tau_4 t_4 \dots = 0$$

$$\tau_1 t_1^2 + \tau_2 t_2^2 + \tau_3 t_3^2 + \tau_4 t_4^2 \dots = 0$$

$$\tau_1 t_1^3 + \tau_2 t_2^3 + \tau_3 t_3^3 + \tau_4 t_4^3 \dots = 0$$

$$\tau_1 t_1^4 + \tau_2 t_2^4 + \tau_3 t_3^4 + \tau_4 t_4^4 \dots = 0$$

$$\dots = 0$$

Then, unless  $\tau_1 \tau_2 \tau_3$  &c. are all zero, we have

$$\begin{vmatrix} t_1 & t_2 & t_3 & t_4 & \dots \\ t_1^2 & t_2^2 & t_3^2 & t_4^2 & \dots \\ t_1^3 & t_2^3 & t_3^3 & t_4^3 & \dots \\ t_1^4 & t_2^4 & t_3^4 & t_4^4 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0$$

$$\text{or } t_1 t_2 t_3 t_4 \dots (t_1 - t_2)(t_1 - t_3)(t_2 - t_3)(t_1 - t_4) \dots = 0.$$

Hence one of these factors must be zero, and therefore by symmetry all in the same group; that is, either all the thicknesses of the layers are zero, or all are equal; and in the latter case we get

$$\tau_1 + \tau_2 + \tau_3 + \tau_4 \dots = 0,$$

or the sum of the densities in one cap is equal to that in other.

Mr. Fisher nearly came to this point when he supposed his  $n$  quantities  $t_1 t_2$ , &c. to be connected by  $n-1$  equations. If he had only tried  $n$  equations instead he would have come to this same result. It may be noted that the first  $n$  equations (B) give us  $t_1 = t_2 = t_3$ , &c., and hence any number of such equations will be satisfied, for they all reduce to

$$\tau_1 + \tau_2 + \tau_3 + \tau_4 \dots = 0.$$

Now since the supposed layers of each cap overlap—for I admit that my second objection is answered and that this is assumed in the working—and they are all equal, the division of the cap into coincident layers of different density is quite arbitrary, provided the sum of the densities of the parts is the same in the two caps. Equations (B) mean, therefore, that the two caps are identical in all respects. In other words, we get to the following curious result, that Mr. Fisher's mathematical argument, if assumed to be correct, would show that identical attractions can only be produced by identical

caps ; *i.e.*, would prove that his hypothesis is wrong, when he assumes that gravitation is constant in spite of the different densities of the oceans and continents.

A second paper by the same author\*, in reply to another criticism of his conclusions as to the existence of a level of no strain at a small depth below the earth's surface, calls for a few observations.

It is certainly a gain to have elicited that, by Mr. Fisher at least, "no claim is made that such a change in condition exists at that depth in the actual earth." I thought that a level of no strain had been "discovered," and that its actual position in the earth was "proved" to be at so slight a depth as to show that the surface-features had been produced by some other cause than contraction, notwithstanding its presence.

Somehow or other, however, my two objections have got mixed. The *a priori* objection is that in *any* cooling globe such a level in such a position is extremely unlikely; and the *a posteriori* objection is that "in that case the surface-features would not have resembled . . . those that we see," which is thus admitted by Mr. Fisher. That this objection does not simply involve a *petitio principii* may be seen from the fact that the compression at the poles is neglected in the investigation, and this would make a difference two or three times as great as the supposed depth of the level of no strain.

But, as Mr. Fisher says, the primary objection is to the method, and I am much obliged to him, and I think others will be also, for calling attention to the investigation of the question by Prof. R. S. Woodward, which is an admirable piece of work, though I do not see that it helps Mr. Fisher much. Prof. Woodward distinguishes between "free cooling," which is considered by Lord Kelvin and Mr. Fisher, and "conditioned cooling," which was dealt with by Poisson, Fourier, and Riemann, and which is the actual state of affairs with regard to the earth; and he gives this curious reason for assuming that the former may be adopted instead of the latter, that "defects in the best data at present attainable, and probable inaccuracies in our fundamental assumption, render the results uncertain even in the first place of decimals." In other words, when applied to the actual earth, both suppositions must give such loose approximations that it matters little which is taken. How, then, can we hope to get results of any value when we deal with such small quantities as a mile or two in a spheroidal earth?

But, more than this, it seems to me that as soon as

\* Phil. Mag. July 1894.

Mr. Fisher leaves his guide his equations become wrong. The formula given by Prof. Woodward for the temperature  $u$  becomes indeterminate when we make  $x=r$ , i. e. when we seek to know the temperature at the centre, as the expression in brackets becomes zero; and to this there is no objection. But when Mr. Fisher takes only the first two terms and differentiates, he gets

$$\frac{du}{dt} = -\frac{V}{\sqrt{\pi}} \frac{r}{r-x} \frac{x}{t\sqrt{4\kappa t}} e^{-\frac{x^2}{4\kappa t}}.$$

If in this we put  $x=r$ , and  $r$  is not infinite, then  $\frac{du}{dt}$  becomes infinite—that is, the rate of cooling at the centre is infinite—while in reality it must be quite small. In like manner  $\frac{du}{dx}$  also becomes infinite, i. e. the temperature at the centre is infinitely greater than elsewhere. As Mr. Fisher's results depend on the values of these differential coefficients, it does not seem possible that they can be correct.

If the mathematics is to teach us anything we must keep the meaning of our equations well in mind throughout. As I have shown, each term of the series which satisfies the fundamental equation

$$\frac{d(zu)}{dt} = \kappa \frac{d^2(zu)}{dt^2}$$

gives the cooling greatest at the centre, and the sum of a number of maxima must itself be a maximum. Hence, if we do not discriminate in some way, it would follow that throughout the whole cooling from  $t=0$  to  $t=\infty$  the cooling is greatest at the centre; whereas we know very well that at the beginning the cooling will be greatest at the surface. This must be accounted for in some way, whether my explanation of it be correct or not; in fact, in the cooling of every body there must be two stages—the first, a temporary one, when the exterior cooling is most rapid, and the second, one which lasts till all the heat is lost, during which time the surface has so little heat to lose that the centre cools quickest; and the question is whether the earth has now, and, if so, when it, entered on this second stage.

Only when the temperature condition of the earth is settled can we enter into the question of its results as regards contraction and a level of no strain. There appears to me to be an error also in Mr. Fisher's investigation of this point, as he deals with the *circumference* of the earth at the level he discusses rather than with the *spherical area*; but as we do

not really reach this point, I have not entered into that question, nor do I desire to do so.

It does not appear, therefore, that the mathematical investigation prevents us in any way from taking a general view of the matter under the light of the positive teachings of geology. We know that a cooling body must contract, and that it will not contract equally throughout; we know that the surface-features demonstrate a great amount of contraction, and whether other causes of contraction have operated or not, we are at liberty to look on the cooling as one of the most potent; and geological observations must teach us how far and in what manner such contractions have been effected.

### XLIX. Of the "*Electron*," or Atom of Electricity.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

PROFESSOR EBERT, in his paper on the Heat of Dissociation in last month's (September) Phil. Mag., says on p. 332:—"Von Helmholtz, on the basis of Faraday's Law of Electrolysis, was the first to show in the case of electrolytes that each valency must be considered charged with a minimum quantity of electricity, the 'valency-charge,' which like an electrical atom is no longer divisible."

Now I had already twice pointed out this remarkable fact: first, at the Belfast meeting of the British Association in August 1874, in a paper "On the Physical Units of Nature," in which I called attention to this minimum quantity of electricity as one of three\* physical units, the absolute amounts of which are furnished to us by Nature, and which may be made the basis of a complete body of systematic units in which there shall be nothing arbitrary. This same paper was again read before the Royal Dublin Society on the 16th of February, 1881, and is printed both in the Proceedings of that meeting and in the Phil. Mag. of the following May.

\* The two other units being (1) the "*Maxwell*" of velocity, that velocity which connects electrostatic with electromagnetic units in a medium of which the inductive capacity is unity, and which, under the electromagnetic theory of light, is also the maximum velocity of light; and (2) the "*Newton*" of gravitation, that coefficient of universal gravitation of the amount of which Professor Boys has lately made so accurate a determination.

Professor Helmholtz's announcement was made in his Faraday Lecture delivered on the 5th of April, 1881, subsequent to both the announcements I had made. See the Journal of the Chemical Society for 1881. The announcements as made by him and by myself are as follows :—

G. Johnstone Stoney in Aug. 1874, and again in Feb. 1881.

Professor von Helmholtz in April 1881.

"And, finally, Nature presents us, in the phenomenon of electrolysis, with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear I shall express 'Faraday's Law' in the following terms, which, as I shall show, will give it precision, viz. :—*For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases.* This definite quantity of electricity I shall call  $E$ . If we make this our unit quantity of electricity, we shall probably have made a very important step in our study of molecular phenomena."

"Now the most startling result of Faraday's Law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity. As long as it moves about on the electrolytic liquid each ion remains united with its electric equivalent or equivalents. At the surface of the electrodes decomposition can take place if there is sufficient electromotive force, and then the ions give off their electric charges and become electrically neutral."

(Readers of my paper are requested to bear in mind that it was written so long ago that the Ampère was still understood to mean the electromagnetic unit *quantity* of electricity of the Ohm series. The term is now always applied to the unit *current*. Moreover the paper, having been written before C.G.S. units came into use, employs those which had been at an earlier date adopted by the Committee of the British Association on Electrical Standards, viz. the G.M.S., or gram-metre-second system.)

In this paper an estimate was made of the actual amount of this most remarkable fundamental unit of electricity, for which I have since ventured to suggest the name *electron*. According to this determination the electron = a twentietheth (that is  $10^{-20}$ ) of the quantity of electricity which was at that time called the ampere, viz.: the quantity of electricity which passes each second in a current of one ampere, using this term here in its modern acceptance. This quantity of electricity is the same as three eleventhths ( $3 \times 10^{-11}$ ) of the C.G.S. electrostatic unit of quantity.

That determination was made twenty years ago, and is founded on the estimate I had previously announced in 1867 of the number of molecules present in a gas, viz.:  $10^{18}$  in each cubic millimetre of a gas at standard temperature and pressure (see Phil. Mag. for August 1868, vol. xxxvi. p. 141).

An estimate of this same remarkable unit of electricity was made in 1891 by Professor Richarz, as quoted by Professor Ebert (see p. 335 of the September number of the Phil. Mag.). His determination makes the electron =  $12.9$  eleventhets ( $12.9 \times 10^{-11}$ ) of the C.G.S. electrostatic unit. This appears to be in sufficiently satisfactory agreement with my previous determination, having regard to the amounts of the probable errors of some of the data.

Finally, in 1891 (see Transactions of the Royal Dublin Society, vol. iv. p. 583), I called attention to the fact, which Professor Ebert appears also to have noticed in 1893 (see footnote on p. 335 of the September number of the Phil. Mag.), that the motions going on within each molecule or chemical atom cause these electrons to be waved about in the luminiferous æther, and that in this constrained motion of the electrons the distinctive spectrum of each kind of gas seems to originate: since lines in the spectrum will be furnished by each term of the Fourier's series which represents the special motion of each electron (see Transactions of the Royal Dublin Society, vol. iv. 1891, p. 585). In fact the only other conceivable source of these spectra is excluded, viz., Hertzian undulations consequent upon electric discharges within or between the molecules. This is because these undulations, if they exist, must consist of waves of far too high frequency to produce lines that can be visible, or even that could be situated within any part of the spectrum that has been reached by photography—a circumstance to which my attention was called by Professor FitzGerald. They cannot, therefore, be the cause of any part of the *known* spectra of gases.

I am, Gentlemen,  
Yours faithfully,  
G. JOHNSTONE STONEY.

8 Upper Hornsey Rise, N.  
September 4, 1894.



L. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 245.]

April 11th, 1894.—Dr. Henry Woodward, F.R.S.,  
President, in the Chair.

THE following communications were read :—

1. 'Mesozoic Rocks and Crystalline Schists in the Lepontine Alps.' By T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S., Professor of Geology in University College, London, and Fellow of St. John's College, Cambridge.

The author described the results of an examination of the infold of Jurassic rock in the Urserenthal, undertaken in the hope of finding some definite evidence as to the relations of the marble, exposed near the old church at Altkirche, and the adjacent Jurassic rocks. Good sections are few and far between; for the comparatively perishable nature of the rock causes it usually to be masked by débris and turf.

The easternmost of the sections described occurs high up on the slopes north of the Oberalp road. Read off from the northern side it exhibits (1) gneiss, (2) phyllites with bands of subcrystalline limestone, etc.—Jurassic, (3) a little rauchwacke, (4) 'sericitic' gneiss. The next section (about 250 feet above the St. Gotthard road at Altkirche) gives (1) gneiss, (2) covered ground, (3) slabby marble, (4) phyllite, (5) thicker mass of slabby marble, (6) phyllite, etc., (7) 'sericitic' gneiss. The third section (just above the church) runs thus, using numbers to correspond with the last :—(1) gneiss, (4) phyllite, (5) slabby marble, (6) phyllite, etc., (7) 'sericitic' gneiss. It must be remembered that on the slopes of the Oberalp farther south, between the 'sericitic' gneiss and the 'Hospenthal Schists,' another dark phyllite is found, generally considered by the Swiss geologists to be Carboniferous. The marble in the third section is in places distinctly banded with white mica, and passes on the northern side into fairly normal mica-schist and quartzose schist. The fourth section, about a mile away, on the left bank of the Reuss valley, gives a practically continuous section in phyllite and dark limestone, without any marble. In the fifth section, rather more than a mile farther, if any marble is present, it is very thin and shattered. At Realp, about  $3\frac{1}{2}$  miles farther, the next good section is obtained. Here the rocks go in the following order (from the northern side) :—(1) gneiss; (2) phyllite and limestone; (3) subcrystalline limestone, looking very crushed; (4) the marble; (5) phyllite, etc.; (6) Hospenthal Schists. The last group of sections occurs near the Furka Pass. In the first, crossed by the high road, there is no marble, but a little rauchwacke on the southern side. The next one, on the slopes below the pass, seems to show two masses of the marble parted by a subcrystalline limestone like that at Realp, with phyllite above and below. Of the two masses of marble

the southern one can be traced right across the pass, but the extent of the other is not so clear.

Examination of the marble mentioned above shows in all cases that it has been considerably modified by pressure since it became a crystalline rock. The author discusses the evidence of these sections, and maintains that the hypothesis that the marble is an older rock intercalated by thrust-faulting among Jurassic strata leads to fewer difficulties than to consider it as belonging to the same system.

In the latter part of the paper the results of a re-examination of the ravine-section in the Val Canaria, and of some studies of the south side of the Val Bedretto are described, which, as the author maintains, confirm the view already expressed by him, viz., that the schists with black garnets, mica, kyanite, dolomite, and calcite (the last sometimes becoming marbles) are not altered Jurassic rocks but are much older.

2. 'Notes on some Trachytes, Metamorphosed Tuffs, and other Rocks of Igneous Origin, on the Western Flank of Dartmoor.' By Lieutenant-General C. A. McMahon, F.G.S.

In this paper the author notices the occurrence of felsite and trachyte at Sourton Tor; of rhyolite and of aluminous serpentine at Was Tor; and of a dolerite at Brent Tor in the exact situation indicated by Mr. Rutley as the probable position of the throat of the Brent Tor volcano.

The author describes extensive beds of tuffs at Sourton Tor and Meldon, the matrix of which has been converted, by contact-metamorphism, into what closely resembles the base of a rhyolite, and which, in extreme cases, exhibits fluxion-structure, or a structure closely resembling it. The fragments included in this base are so numerous that six or seven different species of lavas may be seen in a single slide; this fact, and a consideration of the extensive area over which these beds extend, lead the author to believe that these beds are metamorphosed tuffs and not tufaceous lavas.

He then describes some beds on the flank of Cock's Tor, which give evidence on their weathered surface of an original laminated structure by exhibiting a corded appearance like corduroy cloth. These beds are composed of colourless augite, set in a base which in ordinary light looks like a structureless glass, but which between crossed nicols is seen to be an obscurely crystalline felspar.

The author compares these rocks with that portion of the Lizard hornblende-schists for which a tufaceous origin was proposed by De la Beche and other writers, including Prof. Bonney and himself. He shows that the Lizard schists and the Cock's Tor rocks agree in specific gravity and in some other characteristics; and he concludes that at Cock's Tor the first stage in the conversion by contact-action of beds of fine volcanic ash into hornblende-schist had been completed, and the final stage, due to aqueous agencies, had just begun.

The paper concludes with some remarks on the relationship of the epidiorites to the rocks of volcanic origin.

April 25th.—Dr. Henry Woodward, F.R.S.,  
President, in the Chair.

The following communications were read:—

1. 'Further Notes on some Sections on the New Railway from Romford to Upminster, and on the Relations of the Thames Valley Beds to the Boulder Clay.' By T. V. Holmes, Esq., F.G.S.

The author alludes to his discovery of Boulder Clay on this new railway at Hornchurch (dealt with in a previous paper, Q. J. G. S. Aug. 1892), and describes the finding of more Boulder Clay close to Romford during the deepening and widening of a cutting there. The Boulder Clay was on precisely the same level as that at Hornchurch, a mile and a half to the south-east, and, like it, was covered by gravel belonging to the highest, and presumably oldest, terrace of the Thames Valley system. A portion of the silted-up channel of an ancient stream-course was also found in this Romford cutting. Its relations to the Boulder Clay could not be seen, as they were not in contact, but they were alike covered by the oldest gravel belonging to the Thames Valley system. The author discusses the probable direction of the flow of this stream-course, and the way in which it was superseded by the ancient Thames. After noticing certain points brought forward during the discussion on his former paper, he concludes with a criticism on the views to which Dr. Hicks inclines in his paper on the Sections in and near Endsleigh Street (Quart. Journ. Geol. Soc. vol. xlviii. 1892) as regards the age of those beds, asserting that they are, in all probability, simply River Drift of the Thames Valley system, and consequently post-Glacial, in the sense of being later in date than the Boulder Clay of Essex and Middlesex.

2. 'On the Geology of the Pleistocene Deposits in the Valley of the Thames at Twickenham, with Contributions to the Flora and Fauna of the Period.' By J. R. Leeson, M.D., F.L.S., F.G.S., and G. B. Laffan, Esq., B.Sc., F.G.S.

The section described in this paper was exposed during the construction of an effluent from the Twickenham sewage-works to the Thames. Its length was about one mile.

The beds exposed were:—(1) Coarse reddish-yellow gravels, coloured blue below, lying on an eroded surface of (2) Dark blue loam, varying in thickness, the greatest thickness seen being 3 feet, at a place where the bottom was not reached; (3) Dark sand; (4) Coarse ballast-gravel; (5) London Clay.

The loam (which is quite a local deposit) yielded 8 species of mollusca and 14 species of plants, all still living in the neighbourhood. A number of mammalian bones referable to 7 species were lying just on the surface of the loam. Amongst the forms were bison and reindeer.

The authors consider that the loam was deposited in a small lake, and they allude to similarities between it and a deposit described by Dr. Hicks as occurring in the Endsleigh Street excavations.

3. 'On a new *Goniatite* from the Lower Coal Measures.' By Herbert Bolton, Esq., F.R.S.E.

## LI. *Intelligence and Miscellaneous Articles.*

### A STUDY OF UNIPOLAR INDUCTION.

BY PROF. DR. ERNST LECHER.

THE first part contains historical and general observations, and shows that neither previous experiments nor the more recent modifications can settle this question. It appears that the Biot-Savart law, of the action of a rectilinear conductor on a magnetic pole, is not in harmony with experimental facts.

The second part contains a condensed account of the experiment of an electrometric proof of electrostatic charges of a rotating magnet. The author does not consider these experiments to be free from objection.

The third part contains the *experimentum crucis*, and the decision of the question raised. A magnet is divided by an equatorial section in two parts, each of which can rotate separately. By means of suitable spring contacts it is possible to obtain from the two ends of the magnet an induction current which cannot possibly be due to a cutting of the rotating lines of force in the short fixed spring contacts. The current is easily explained if we adopt the view of Faraday, which, however, he afterwards abandoned, that the rotating magnet cuts its own fixed lines of force, and thus has an electromotive action.—*Wiener Berichte*, July 12, 1894.

### ON THE CIRCULAR MAGNETIZATION OF IRON WIRES.

BY PROF. DR. IGN. KLEMENČIČ.

The author investigated, in wires of soft and hard iron and of Bessemer steel, the extra currents which are formed on passing a current owing to circular magnetization. From the extra currents the susceptibility in a circular direction may be calculated by a formula of Kirchhoff. The susceptibility in an axial direction for different field-strengths was determined. The experiments showed that qualitatively the course of the susceptibility in both directions is pretty much the same. Quantitatively, however, the following difference is to be observed. With soft-annealed iron the susceptibility about the axis is less than in the direction of the axis. If the iron wire is hardened by a stress, the susceptibility in a longitudinal direction diminishes more rapidly than in the circular, and the behaviour observed for soft iron may even be reversed.

Simultaneous experiments on remanent magnetism gave greater values for this with circular than with axial magnetization, especially in hard iron and steel. Repeated demagnetization with greater field-strengths increases the susceptibility for weaker fields, even with circular magnetization.—*Wiener Berichte*, July 5, 1894.

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JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

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NOVEMBER 1894.

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LII. *Wave-Lengths of Electricity on Iron Wires.*  
By CHARLES E. ST. JOHN, A.M.\*

[Plate XII.]

THE question whether the magnetic properties of iron are called into play under extremely rapid alternations of the magnetizing forces is an interesting one, and has received various answers.

Hertz found negative results when he replaced one side of a rectangular copper resonator† by an equal iron wire; and in a later paper, on the “Finite Velocity of Electromagnetic Action”‡, when he compares the rate of propagation along copper and iron wires, he concludes “that the rate of propagation in all wires is the same, and we are justified in speaking of it as a definite velocity. Even iron wires are no exception to this general rule; hence the magnetic properties of the iron are not called into play by such rapid disturbances”§.

Dr. Oliver J. Lodge attacked the question by means of his experiment on the alternate path. In his ‘Lightning Conductors and Lightning Guards’ (1892), he remarks:—“But everyone will say—and I should have said before trying—surely iron has more self-induction than copper. A current

\* Communicated by Prof. J. Trowbridge.

† Wied. Ann. xxxi. p. 429 (1887). ‡ Ibid. xxxiv. p. 351 (1888).

§ ‘Electric Waves,’ p. 113.

going through iron has to magnetize it in concentric cylinders, and this takes time. But experiment declares against this view for the case of leyden-jar discharges."

Prof. John Trowbridge has shown\* that the magnetic character of iron wires exercises an important influence upon the decay of electrical oscillations of high frequency, and that currents of such frequency as occur in leyden-jar discharges magnetize the iron. The spark in geometrically similar oscillating circuits of copper and iron was photographed by means of a revolving mirror, and the number of oscillations on the negatives compared.

Prof. J. J. Thomson has shown† that the presence of iron can affect the rapidly oscillating electric discharges through a rarefied gas by absorbing the energy of the discharges.

In a paper upon the "Absorption Power of Metals for the Energy of Electric Waves,"‡ V. Bjerknes has also given results that prove the great damping power of magnetic metals upon electric oscillations of very high frequency (100,000,000 double oscillations per second).

If the damping power of iron is due to the fact that its magnetic properties are brought into play under such rapidly alternating forces, it still remains an interesting question whether the self-induction of an iron circuit is measurably greater than that of a similar copper circuit, and whether the wave-length remains constant for oscillations of the same period.

In the determinations of the wave-length due to the Hertzian vibrator, the arrangement originated by Hertz§, and modified by Lecher|| and by Sarasin and De La Rive¶, has been very generally employed. In this arrangement secondary disks were placed face to face with the plates of the vibrator and near to them, to each secondary disk a long wire was attached, and these wires carried through the air parallel to each other, with, sometimes, an additional disk on the free ends.

With such an arrangement no exact adjustment of the length of the secondary circuit was required in order to excite powerful oscillations in it, for the direct electrostatic induction

\* 'Proceedings of American Academy of Arts and Sciences,' xxv., May 27, 1891.

† Phil. Mag. [5] xxxii. p. 456, July 1891.

‡ Wied. Ann. xlv. p. 74 (1891).

§ Ibid. xxxiv. p. 551 (1888).

|| Ibid. xli. p. 850.

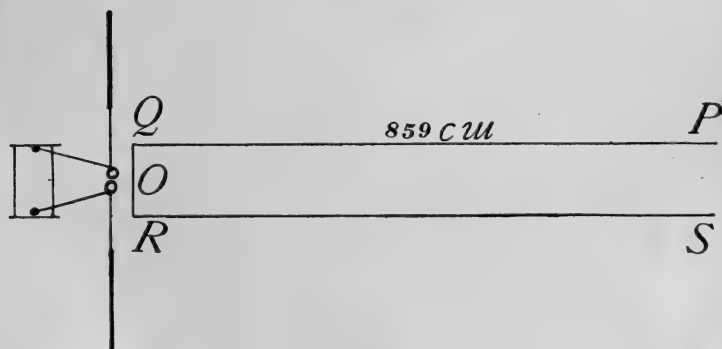
¶ Archives des Sciences Physiques, t. xxiii. p. 113 (1890).

between the plates of the secondary and the disks on the ends of the primary wires was so great that vigorous oscillations were produced along the secondary wires whatever their length might be, and several systems of waves could be detected which seemed to give experimental grounds for believing that the wave-system sent out from the Hertzian vibrator was very complex.

The capacity of the vibrator is increased by the presence of these secondary disks so near to the vibrator-plates, so that the wave-length found under these conditions is not that due to the simple Hertzian vibrator but that due to a very complex oscillating system with somewhat obscure internal reactions. Especially is this true when the wires are bridged as in the Lecher arrangement. The latter calls attention to the change in the sound of the primary spark when the secondary wires are bridged by a conductor. There is a very marked difference in the spark when the secondary circuit is removed entirely: the spark then loses much in body and explosive character. The secondary circuit under these conditions exerts apparently a strong reaction upon the primary.

It seemed desirable to devise some form of secondary depending more directly upon the principle of electrical resonance, the use of which would not increase the capacity of the vibrator, and whose reaction upon it would be a minimum. This was done by omitting the secondary disks and using simply a long wire as shown in fig. 1.

Fig. 1.

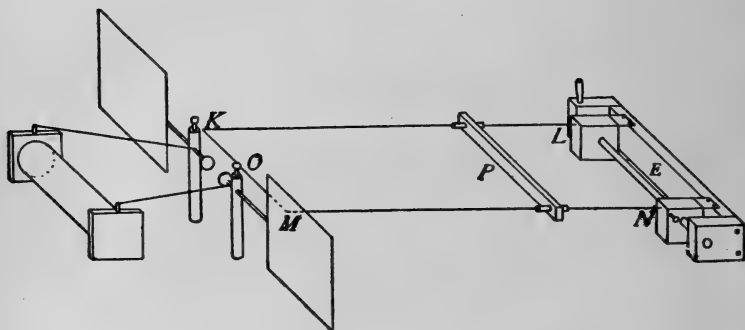


The secondary circuit consists of the long rectangle PQRS,

which is carefully adjusted to resonance before any other measurements are made.

For determining the occurrence of resonance and for exploring the wires to obtain the wave form, the bolometer as described by Paalzow and Rubens\* was used in connexion with Rubens's † adaptation of it. The exploring terminals of the bolometer are shown at P, fig. 2. They consist of two

Fig. 2.



capillary glass tubes set in a frame of wood; the tubes slide over the wires to be explored, and around each tube is wrapped, by a single turn, one of the lead wires to the bolometer. Electric oscillations in the secondary circuit cause inductively alternating currents along the lead wires through one arm of a balanced Wheatstone bridge, which forms the bolometer. This arm of the bridge is made of fine iron wire, and so arranged that the bridge current and these oscillating currents traverse it without affecting each other. The bridge is thrown out of balance by the increase of resistance caused by the heat generated from the alternating currents, and a corresponding throw of the galvanometer is produced.

To adjust the circuit to resonance the exploring terminals were placed at P S (fig. 1). The induction-coil was put in action, and the reading of the bolometer taken for this length of wire. A few centimetres of wire were cut off and the reading again taken. This operation was repeated until a maximum

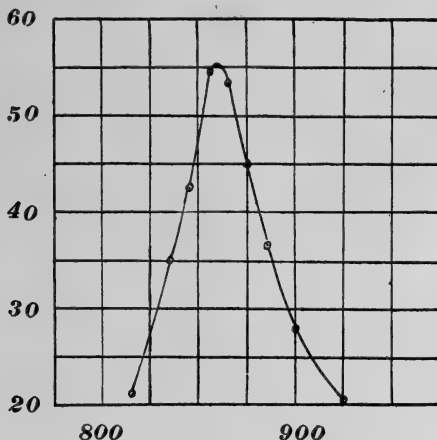
\* "Anwendung des bolometrischen Principis auf electriche Messungen," Wied. *Ann.* xxxvii. p. 529.

† "Ueber stehende electriche Wellen in Drähten und deren Messung," *Ibid.* xlii. p. 154.



point was passed. The wires were renewed, and the operation repeated again and again. A sharp and unmistakable maximum was found when P Q was 859 centim. long. (fig. 3). The effect fell off rapidly either when the wires were lengthened or shortened from this point. The result is shown graphically in fig. 2 (Pl. XII.), where distances from Q are used as abscissas and deflexions of the galvanometer as ordinates. When the

Fig. 3.



circuit is thus arranged, there is little effect produced upon it by the vibrator unless it is near the point of resonance. The period of the vibrator is the controlling factor, and the influence of the secondary circuit is greatly reduced.

To determine the character of the vibration along the wire, the lengths Q P and R S (fig. 1) were fixed at 859 centim., the exploring terminals were moved along the rectangle, and the bolometer-readings taken for each position of the exploring terminals. The graphic representation of the results is given in fig. 1 of Pl. XII., where, as in all the curves, the abscissas are the length of the sides of the rectangle and the ordinates the bolometer-readings. The character of the curve indicates a simple form of vibration. The total length of the wire is equivalent to 7 half wave-lengths. The minimum points occur at nearly equal intervals, and the distance from the minimum at 748 centim. to the centre O (fig. 1) of the side Q R may be taken as 3 half wave-lengths. This furnishes a ready means of calculating the half wave-length.

$QR = 30$  centim.  $748 + 15 = 763$  centim.  $763 \div 3 = 254.3$  centim. = a half wave-length. The distance from this minimum to the end of the wire P should be a fourth wave-length of 127.15 centim. The actual distance is  $859 - 748 = 111$  centim., so that the correction for the free end of the wire is about 16 centim.

To adjust the length of the wire under this arrangement was a work of considerable difficulty, but the possibility of using a single-wire circuit free from disturbing capacities overbalanced much inconvenience. To remove some of this, the ends P and S were wound upon wooden bobbins, so that shortening and lengthening could be produced without cutting the wire. This was a marked gain in convenience; but the changing size and form of the coils, as the wire was shortened or lengthened, altered the capacity at the end slightly and somewhat irregularly. This led to the adoption of the arrangement shown in fig. 2.

The secondary circuit consists of the rectangle K L M N with the side L N open; the lengths of the sides K L and M N can be varied between 15 centim. and 1000 centim. The ends are really formed by the small copper boxes L and N. These were 10 centim. square and 4 centim. thick, and mounted upon the wooden bar E by insulating supports. Within the boxes were wooden bobbins fixed on a hard rubber axle, and each capable of holding 10 metres of the largest wire experimented upon. In the front of each box was a small opening for the passage of the wire, but, to insure a firm contact between the wire and the boxes, a brass block was soldered on the inner side of the front and a binding screw passed in from the side of the box. The bar E was fastened to a wooden support resting upon a car which ran on a wooden track extending the entire length of the room. The car carried a brake so that the wires could be drawn taut, and the wooden screw held the axle from turning. With this arrangement the length of the wire could be varied at pleasure while the end capacities remained constant.

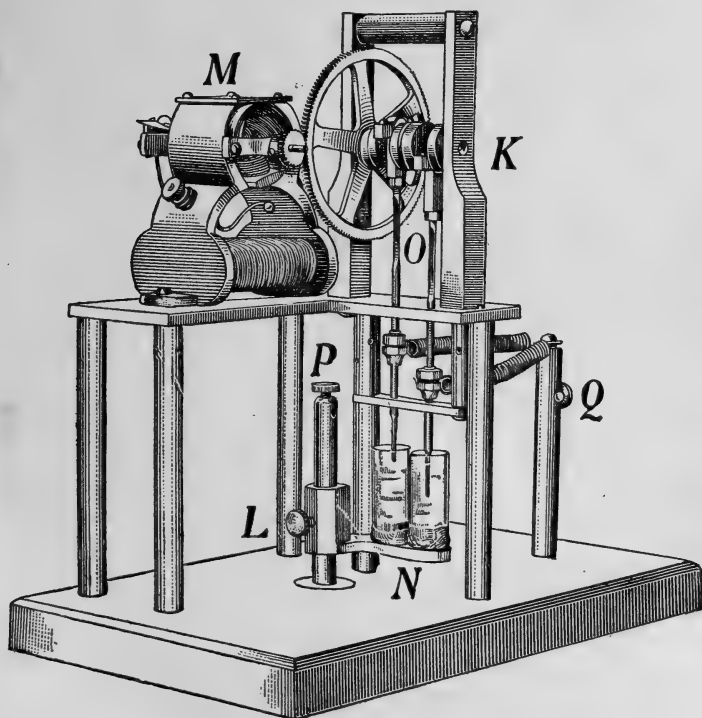
The end capacities are not a desirable feature, for their own sake, since they destroy the perfect simplicity of the plain rectangular circuit, and seem to detract somewhat from the sharpness of the maxima; but the gain in convenience and the possibility of obtaining a large number of observations whose average values can be used may overbalance these considerations.

For making and breaking the current through the induction-coil, an interruptor which would work with certainty and

regularity was much needed. With the assistance of the mechanician of the laboratory I devised an interruptor which gave very satisfactory results.

A small electric motor *M* (fig. 4) was used to produce the necessary motion. This was actuated by the current from two storage-cells, and ran at a fairly constant speed. The armature of the motor was in three sections, and was free from dead points, giving it the great advantage for the present purpose that it could be set in action simply by closing the circuit, making it possible to control it from the observer's station.

Fig. 4.  $\frac{1}{4}$  Scale.



The motor was geared to the two-crank shaft *K* by means of a wheel and pinion. The speed of the shaft *K* was about 750 revolutions per minute, so that about 25 breaks were made per second. The plunging-rods were thinned at *O* so that

they were flexible and gave the required freedom of motion. They ran through the bed-plate and the brass bar below, which served as guides. The plunging-rods carried bind-screws by which the flexible coils leading the current from the brass post Q were attached. The lower ends of the plungers were of No. 18 platinum wire. The brass bottoms of the glass mercury-cups screwed into the brass arm N, which was adjustable by means of the collar and binding-screw L along the pillar P. At P was attached one pole of the battery actuating the coil and also one pole of the condenser in the base of the coil, and at Q was attached one pole of the coil and the other pole of the condenser. The cups were filled with mercury to a height of 8 millim. and then filled with alcohol to within a few millimetres of the top. They usually required cleaning only after several hours' use, when the surface of the mercury consisted of very fine globules, and sharp breaks were not made at each stroke of the plunger as was indicated by the occasional failure of the spark. The character of the spark depended much upon the exact height of the mercury-cups. The adjustment was best made while the coil was in action by raising or lowering the cups until the spark had a white body and a peculiar snap.

The plates of the Hertz vibrator were 40 centim. square and fixed at 61 centim. apart. The spark-gap was supplied with platinum-faced balls (3 centim. in diameter), which worked with less trouble than the usual brass ones. The side K M (fig. 2) of the secondary circuit was parallel to the conductor forming the vibrator plates, and fixed at 6 centim. distance with its centre O opposite the spark-gap. The long sides of the rectangular secondary lay in a horizontal plane, and ran through the centre of the room at a height of 1.6 metre above the floor. They were held by their end supports at 30 centim. apart. The induction-coil was 53 centim. long, 19 centim. in diameter, and was excited by the current from five storage-cells. A sparking distance of about 6 millim. was most effective in producing oscillations in the secondary circuit.

The following method was pursued in taking the observations. The interruptor was set in action, the circuit closed through the induction-coil, and an observation taken of the first swing of the needle. The circuits were broken as soon as the needle reached the end of its first swing, and the extent of this excursion was the reading recorded. In accordance with the experience of Paalzow and Rubens, it was found that a steady deflexion could not be obtained, but this first

swing was, under like conditions, satisfactorily constant; and a preliminary calibration of the instrument by passing currents of known strength through it, showed that the square root of the deflexion taken in this manner was in a constant ratio to the current.

The same copper wire (diameter 0.1201 centim.) that had been used in the secondary without end capacities was used for the rectangle K L M N in fig. 2, and, with the exploring terminals close to L and N, the maximum point was found by lengthening and shortening the wire. Bolometer-readings were taken for each length used. To insure the constant activity of the spark, a convenient length was taken as a point of reference, and observations taken at this point before and after a series of readings. If the spark had remained constant, the readings were retained. A maximum point was found when K L was 818 centim. The sides were fixed at this length, and the form of the wave was obtained by sliding the exploring terminals along the wire, and taking bolometer observations for each position. The result is shown in fig. 3 of Pl. XII. The critical points were determined several times, and the steadiness of the spark insured by choosing, as before, a point of reference. The curve shows three minima at 240, 496, and 752 centim., starting from O. These give half wave-lengths of 255, 256, and 256 centim., with an average of 255.6 centim. The third minimum at 752 centim. was determined with care, as it was to be used as a basis for calculating the half wave-length. An error in determining the position of this minimum would be divided by three, since the distance from O to this minimum was three half wave-lengths. The total length of the circuit was seven half wave-lengths, and it was the equivalent of one fourth of a wave-length from the third minimum to the end. The actual distance to the end was  $818 - 752 = 66$  centim.  $127.8 - 66 = 61.8$  centim. = the equivalent of the capacities in centimetres of wire.

A comparison of the curve (fig. 1, Pl. XII.) obtained from the plain wire circuit with the curve (fig. 3) obtained when capacities were fixed on the free ends, shows a quite satisfactory agreement, which tends to create confidence in both methods. The half wave-length by the first is 254.3 centim. and by the second it is 255.6, values which differ by about one-half of 1 per cent. There is a marked difference, as was to be expected, in the form of the curve next the free ends. When end capacities were used, the accumulation of charges seemed largely confined to them, out of reach of the

exploring terminals, while with the plain wire it seemed distributed over a greater distance. In each case the effect of the ends was to make the curve depart from the normal form along the free wire.

The theory of my investigations rests upon the principle of electrical resonance. The sides of the rectangle K L M N (fig. 2, p. 428) were shortened to a few centimetres in length, so that it could be safely assumed that the period of the secondary was considerably shorter than that of the vibrator. The exploring terminals were kept at L N, and bolometer observations taken for each small addition to the length of the sides K L and M N. When best resonance was found with the shortest length of the secondary circuit that gave a maximum, it was assumed that the secondary had the same period as the vibrator and that its equivalent length was a half wave-length, its actual length depending upon the effect due to the free ends. The occurrence of resonance is a very marked phenomenon even with a vibrator that damps as rapidly as the Hertzian. The accompanying table shows two series of readings for the first maximum when an iron wire was used :—

Length of sides of rectangle...	15	25	35	40	42.3	45	50	60	75
Deflexions of Galvanometer...	107	145	156	194.3	199.2	181.5	140	81	42
“ “ “ ...	94	119	161	185	191	178	136	76	34

There can be no free motion of electricity at the ends of the secondary circuit, but an accumulation alternately positive and negative, and a resulting alternation of potential, the phase at L being always opposite to the phase at N in case of resonance. Elsewhere along the circuit the electricity moves with more freedom and less accumulation. The point O may be called the electrical middle of the circuit, where the accumulation is least and the movement most unrestrained. The electromotive impulses from the vibrator act directly upon the side K M, so that O remains a point of free motion or the ventral segment of the wave, while L and N are always places of no electric movement, or the nodal points. The shortest circuit being a half wave-length, a second resonating circuit ought to be found by increasing each side of the rectangle by a half wave-length, making the circuit three half wave-lengths long, and a third when the circuit is five half wave-lengths, and so on\*. It is known that the change of period

\* J. J. Thomson, 'Recent Researches in Electricity and Magnetism,' p. 297.

produced by replacing copper by iron does not exceed 2 per cent. The difference in length between a copper and an iron circuit of the same period would be very small with circuits a half wave-length long; but this difference would be three times as great with circuits three half wave-lengths long, and there might be a cumulative difference that would become measurable by the use of circuits of still greater length. To examine this question, a copper wire (diameter 0.1201 centim.) was used as the secondary circuit in fig. 2. The sides were taken 15 centim. long, and gradually lengthened to 875 centim., and bolometer-readings taken for each addition, the exploring terminals being always at the ends L and N. The result is shown graphically by the upper curve in fig. 4, Pl. XII. The critical points in the curve are the results of many separate determinations. The unsteadiness of the spark on the vibrator made the determinations somewhat laborious, though a single series of observations would locate a maximum very closely. After this had been done, the space of about a metre, including the maximum point, was worked over forward and back; the constancy of the spark was insured by choosing a convenient point of reference, as already described.

An examination of the curve shows four maxima occurring when the sides of the rectangle were 45, 306, 562.5, and 818 centim. long. The additions of wire for the successive maxima after the first were 261, 256.5, and 255.5. These should be half wave-lengths. The last two agree well, but the first differs from the average of the last two (256 centim.) by 5 centim. The sides were fixed at 818 centim. and the wave-form, fig. 3 (Pl. XII.), was obtained. From this the half wave-length was found to be 255.6 centim., and the total length of the circuit seven half wave-lengths. By fixing the sides of the rectangle at 562.5 centim. and 306 centim., a similar investigation showed the circuits to be respectively 5 and 3 half wave-lengths long.

An explanation of the fact that the distance between the first and second maxima was anomalously large may possibly be this: for the first maximum the sides of the rectangle were but 45 centim. long, so that the effect of the closed end was relatively great and the maximum appeared earlier than it otherwise would, but when the rectangle was 300 centim. long, the influence of the closed end became relatively small, and the second and future maxima came in the normal positions. Besides, in the first case the capacity was largely local, while in the others it was mainly distributive. This same effect appeared in every case, and seemed a constant phenomenon.

The maximum I omitted from the above discussion was not constantly present, but appeared when the primary spark was especially active, and seems to belong to a circuit whose period is to the period of the vibrator in the ratio of 5:3. The sides of the rectangle were 127.5 centim. long and the end capacities equivalent to 62 centim. of wire. The half wave-length was  $30 + 127.5 \times 2 + 62 \times 2 = 409$  centim.  $409 \div 255.6 = 1.6$  nearly.

This was the only indication of complexity in the vibration of the Hertz vibrator; and it may be explained by supposing that such a vibration is superposed upon the fundamental rate of the oscillator, or that the oscillator when particularly active can excite a circuit having such a ratio to itself. This last seems the simpler, but it is difficult to see why a circuit of the ratio 3:2 should not be excited as well. The maximum I would indicate the presence of an undertone rather than an overtone. This point requires more investigation than it has been possible to give it, and will be left undecided for the present.

An annealed iron wire (diameter 0.1186 centim.) was put in place of the copper, and the same series of observations repeated. The results are shown in the lower curve of the upper pair in fig. 4, Pl. XII. The maxima E F G H appear at 42.5, 301, 553, and 805 centim., in each case before the corresponding maximum with the copper; and the difference is seen to increase with the length of the circuits. The successive additions were 258.5, 252, and 252 centim., the last two agreeing, but the first, as with the copper, is much larger. With the sides of the rectangle fixed at 805 centim., the form of the wave was found as shown in fig. 2 of the plate. The third minimum occurs at 740 centim. Calculated as before, the half wave-length is  $740 + 15 = 755$ .  $755 \div 3 = 251.6$  centim. This agrees well with the value 252 given above by the last two additions, but differs by 4 centim. from the value found when the copper was used.

The same series of observations was repeated with a second pair of finer wires (diameter of copper wire 0.07836 centim., diameter of iron wire 0.0785 centim.). The results are shown in the lower pair of curves in fig. 4 of the plate. A comparison of the curves shows the same general result, which appears more distinctly from the following table:—



	1st Maximum.			2nd Maximum.			3rd Maximum.			4th Maximum.		
	Cu.	Fe.	Diff.	Cu.	Fe.	Diff.	Cu.	Fe.	Diff.	Cu.	Fe.	Diff.
Upper pair...	45	42·5	2·5	306	301	5	562·5	553	9·5	818	805	13
Lower pair...	40	37·5	2·5	300	294	6	552	540	12	799	784	15

The successive differences should be in the ratio of 1, 3, 5, 7, if the theory of the present investigation is correct. The differences for the first two maxima are very small, so that the experimental error in their determination would be relatively large, and in the case of the fourth maximum the damping was so great that it was difficult to fix the point with certainty. The difference for the third maximum was relatively large and the determination of the point was sharp. Taking this difference as a point of reference, the calculated and observed values are shown in the accompanying table:—

	1st Maximum.		2nd Maximum.		3rd Maximum.		4th Maximum.	
	Calcu- lated.	Ob- served.	Calcu- lated.	Ob- served.	Calcu- lated.	Ob- served.	Calcu- lated.	Ob- served.
Upper pair...	1·9	2·5	5·7	5	9·5	9·5	13·3	13
Lower pair...	2·4	2·5	7·2	6	12	12	16·8	15

The observed half wave-lengths for the four wires are :—

- { Copper (diameter 0·1201 centim.) 255·6 centim.
- { Iron ( „ 0·1186 centim.) 251·6 centim.
- { Copper ( „ 0·07836 centim.) 251·6 centim.
- { Iron ( „ 0·07850 centim.) 246·8 centim.

The wires in each pair were as near the same diameter as could be found, the iron of the larger pair having slightly the smaller diameter, but the copper being the smaller one in the second case. In other respects the circuits compared were as nearly identical as possible. The capacity per unit length being the same for wires of the same diameter, the shortening

of the wave-length when iron displaced copper must be caused by an increased self-induction due to the magnetic properties of the iron. This implies that the magnetization of iron can be reversed 115 million times per second. This reduced the "time lag" of magnetization to very narrow limits, if forces of such duration can magnetize the iron.

In the case of extremely rapid oscillations Prof. J. J. Thomson has shown ('Recent Researches in Electricity and Magnetism,' sec. 295) that approximately  $y^2 = \frac{2}{L'C}$ , where  $\frac{y^2}{4\pi^2}$  is the square of the frequency, and  $L'$  is the self-induction for very rapid oscillations and  $C$  the capacity of the system. It is easy from this to calculate an approximate value for the ratio between the self-induction per unit length of the iron and copper circuits.

Let  $L$  = the self-induction of the copper per unit length.

$L'$  = " " " " " iron " "

$C$  = the capacity of either per unit length.

Using as a basis of calculation the data from the third maximum of the curves in fig. 4, Pl. XII., the total length of the copper circuit (diameter 0.1201 centim.) is:—

The sides,  $562.5 \times 2$  . . . . . = 1125 centim.

The closed end . . . . . = 30 "

The equivalent of the end capacities  $62 \times 2 = 124$  "

---

1279 centim.

For the wire (diameter 0.1186 centim.) the length is:—

The sides,  $553 \times 2$  . . . . . = 1106 centim.

The closed end . . . . . = 30 "

The equivalent of the end capacities  $61 \times 2 = 122$  "

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1258 centim.

Since the two circuits have the same frequency, the products of the self-induction and capacity are equal.

$$1258^2 L'C = 1279^2 LC,$$

$$\frac{L'}{L} = 1.034.$$

In the same manner, for

$$\begin{cases} \text{Copper (diameter 0.08840 centim.),} \\ \text{Iron ( " 0.08847 centim.),} \end{cases} \quad \frac{L'}{L} = 1.041.$$

$$\begin{cases} \text{Copper (diameter 0.07836 centim.),} \\ \text{Iron ( " 0.07850 centim.),} \end{cases} \quad \frac{L'}{L} = 1.043.$$

By the use of Lord Rayleigh's formula for inductance under very rapid oscillations, it is easy now to calculate a value for the permeability of the iron.

Lord Rayleigh's formula is:—

$$L' = l \left( A + \sqrt{\frac{\mu R}{2pl}} \right),$$

where  $l$  is the total length of circuit,  $A$  a constant depending only on the form of the circuit, or  $lA$  is the inductance of a similar copper circuit;  $\mu$  the permeability;  $R$  the ohmic resistance;  $p = 2\pi n$ , where  $n$  is the number of complete oscillations per second.

The value of  $p = 2\pi n = 36 \times 10^7$ .

$R$  for iron wire (diam. 0.1186 centim.) = .1328 ohm per metre.

" " " ( " 0.08847 " ) = .227 " "

" " " ( " 0.0785 " ) = .301 " "

For iron (diameter 0.1186 centim):—

$$L' = 1.034 L = l \left( A + \sqrt{\frac{\mu R}{2pl}} \right),$$

$$L + .034 L = L + l \sqrt{\frac{\mu R}{2pl}},$$

$$.034 L = l \sqrt{\frac{\mu R}{2pl}}.$$

Calculating the value of  $L$  for a similar copper circuit  $l$  units long, substituting the value in the above equation, and solving for the three cases, we get:—

For the iron wire, diameter 0.1186 centim.,  $\mu = 430$ ,

" " " 0.08847 "  $\mu = 389$ ,

" " " 0.0785 "  $\mu = 336$ .

These values for the permeability all fall within a reasonable limit, and have for an average  $\mu = 385$ . Those are the values found for different specimens of wire made by the same company, but the specimens were wound and unwound and stretched many times during the series of observations. Besides the shortening of the wave-length there is shown a decided increase in the damping, as has already been observed by Trowbridge and Bjerknes. In fig. 4 (Pl. XII.) the curves for iron fall below the corresponding ones for copper, but owing to the change in the activity of the spark no exact measurement was made. It was only observed that the bolometer throws with the copper circuit were always

greater than with the iron circuit of the same dimensions, when the spark was constant as far the eye and ear could judge.

A value can readily be calculated for the damping factor  $e^{-\frac{Rt}{2L}}$  in the case of the iron and copper. Lord Rayleigh's formula for the resistance under very rapid oscillations is:—

$$R' = \sqrt{\frac{1}{2} p l \mu R}.$$

For the iron wire circuit (diameter 0·1186 centim.),  $l = 1258$ ;  $\mu = 430$ ;  $R = 1·67 \times 10^9$ ;  $p = 36 \times 10^7$ , whence  $R' = 403 \times 10^9$ ,  $L = 34 \times 10^3$ .

The damping factor becomes  $e^{-6 \times 10^6 t}$  approximately.

The time required for the amplitude to fall to one half its maximum value is  $t = 0\ 000000115$  sec. On the basis of  $115 \times 10^6$  alternations per second, the number of complete oscillations during this time is 6·5. A like calculation for the corresponding copper circuit gives about 60 times as many.

The following table shows the results when copper circuits are compared in which wires of different diameters are used:—

				3rd Maximum.
Copper wire	(diameter 0·1201 centim.)			562·5 centim.
" "	( " 0·0884 " )			553·5 "
" "	( " 0·07836 " )			552·0 "
" "	( " 0·03915 " )			535·0 "

The half wave-lengths calculated from this maximum are:—

Copper	(0·1201 centim.)	255·8 centim.
"	(0·0884 " )	252·2 "
"	(0·07836 " )	251·6 "
"	(0·03915 " )	244·8 "

There are found by dividing the total length of the circuit by 5:—

$$535 \times 2 = 1070 \text{ length of sides.}$$

$$30 \quad , \quad \text{closed end.}$$

$$62 \times 2 = \frac{124}{1224} \text{ equivalent of end capacities.}$$

$$1224 \div 5 = 244·8 \text{ centim.} = \text{half wave-length.}$$

The range of wires suitable for the study of the phenomena is rather limited. If the wires have a greater diameter than 1 millim. the difference between iron and copper is slight; while with wires less than 0·5 millim. in diameter the damping is so great that long wires cannot be used, and advantage cannot be taken of the cumulative effect.

I wish to express my great obligation to Prof. John Trowbridge for the encouragement and suggestions that I have received from him.

*Conclusions.*

1. The self-induction of iron circuits is greater than that of similar copper circuits under very rapid electric oscillations ( $115 \times 10^6$  reversals per second). The change in self-induction varies from 3.4 to 4.3 per cent. in the present investigation and increases with decreasing diameters.

2. The increase in self-induction produces greater damping, and a shortening of the wave-length of 1.5 to 2 per cent.

3. The permeability  $\mu$  of annealed iron wire under this rate of alternation is about 385.

4. For oscillations of the same period, the wave-length along parallel copper wires varies directly with the diameter of the wires. (Range of wires used 0.03915 centim. to 0.1201 centim.) The maximum decrease observed is 5 per cent.

Jefferson Physical Laboratory,  
July 24, 1894.

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LIII. *Change of Period of Electrical Waves on Iron Wires.*

By JOHN TROWBRIDGE\*.

IN an investigation upon the damping of electrical waves on iron wires †, I endeavoured to detect a change of periodicity as well as a damping of these waves. On account, however, of the strong damping effect exerted by the magnetic nature of the conductors, not a sufficient number of oscillations could be set up in them to enable one to make conclusive measurements. With more powerful means of experimenting I returned to the subject, and I have detected a marked change in the period of electrical waves which is produced by the magnetic nature of the wire. At the same time Mr. Charles E. St. John, working in the Jefferson Physical Laboratory, by an entirely different method, has shown a change in wave-length on iron wire even for the very rapid period of the Hertz vibrator. It will be remembered that Hertz believed that iron wires behaved like copper wires when transmitting very rapid electrical oscillations. Stefan ‡ in a recent paper gives an analysis of electrical oscillations, in which he proves that rapid electrical waves on iron-wire circuits have the same wave-length as those on copper circuits of the same geome-

\* Communicated by the Author.

† Phil. Mag. Dec. 1891.

‡ Wied. Ann. xli. 1890, p. 422.

trical form—the electrostatic capacity of the two circuits being the same.

With reference, therefore, both to the theory of electrical waves and to the theories of magnetism, it seems important to determine whether there is a lengthening of electrical waves on iron wires.

The method of investigation I employed was the same as that which I have described in my paper on the damping of electrical waves on iron wires. A leyden jar was discharged through the given wires and the resulting spark, spread out by a revolving mirror, was photographed. The apparatus was also modified as I have described in my paper on “Electrical Resonance and Electrical Interference”\*.

It was important in this investigation to be able to compare the times of oscillation on the iron circuits and the copper circuits, and it seemed best to employ some method of imprinting, so to speak, the time of a standard circuit on each photograph, beside the photograph of the spark produced on either the iron circuit or the copper circuit; for if the speed of the mirror changed, this change could be readily detected by the measurements of the oscillations of the standard time-spark. At the first thought it seemed a comparatively simple matter to arrange a suitable time circuit. In Hertz, ‘Electric Waves’ †, appendix p. 271, it is stated:—

“Let the primary coils of two induction-coils be placed in the same circuit, and let their spark-gaps be so adjusted as to be just on the point of sparking. Any cause which starts sparking in one of them will now make the other begin to spark as well; and this quite independently of the mutual action of the light emitted by the two sparks, which, indeed, can easily be excluded.”

I therefore slipped two induction-coils of exactly the same self-induction on a long electromagnet, placing them symmetrically upon it. In the circuits of these induction-coils I placed the same amount of capacity. The spark-gap on the time circuit was made of the same length as that on a circuit of iron or copper wire which was under examination. I expected thus to obtain a photograph of the spark on my standard circuit at the same instant as that of the spark on the trial circuit of iron or copper. To my surprise, I found that the two induction-coils did not respond at the same instant to the impulse in the electromagnet, when the spark-gaps were of the same length. It was necessary to make careful adjustment of these lengths and to modify the amount of

\* Phil. Mag. Aug. 1894.

† ‘Electric Waves,’ Dr. Heinrich Hertz, translated by D. E. Jones, B.Sc.

capacity of the circuits. This want of isochronism may have been due to irregularities in the hard rubber condensers which I employed. This, however, does not seem probable. The condensers were made of sheets of hard rubber one eighth of an inch in thickness, covered with tinfoil, and the set of condensers in the time circuit did not differ geometrically appreciably from the set in the trial circuit. The electrical disturbance on such a connected system is evidently a complicated one when its various reactions are considered, and the statement given by Hertz, which I have quoted, must be modified if there is any capacity in the circuits of the two Ruhmkorf coils which have a common primary.

The capacity in the time circuit was the same geometrically as that in the circuit which included the wires under examination. A suitable amount of self-induction was placed in the time circuit. To ascertain whether the time circuit could be relied upon, I made many measurements of the ratio of the oscillations in the time circuit to those in the trial circuit, which contained copper wires and the same geometrical capacity. I had no reason to suspect a change in the self-induction in my time circuit; a change might occur, however, in the capacity of the indiarubber condensers, due possibly to hysteresis from electric strains and deformations. I could not detect, however, such effects. I was dealing with single discharges, not repeated ones, such as are employed in obtaining wave-lengths along wires, and the photographs of such single discharges showed no evidence of inconstancy in the capacity of my condensers. If there was any effect of electrical hysteresis, it affected my time circuit and my trial circuit alike.

As an example of the degree of accuracy which can be obtained in the measurement of the distances between the oscillations on the negative, the following table is given. The distances between different numbers of oscillations is given in the first column and the average length of the oscillations is given in the third column.

Distance in millim. between the first and last oscillations.	Number of oscillations included in this distance.	Average length of oscillations in millim.
22.5	6	3.75
26.1	7	3.73
30.0	8	3.74
15.1	4	3.77

Repeated measures between the same number of oscillations give closer results ; but one is apt to set the measuring instrument each time on the same points on the negative. It is evident that measuring each time the space between a different number of oscillations gives the fairest result. It is surprising how close one can set the measuring instrument upon the serrations of the negative.

It will be noticed that the ratio between any two determinations of the time on the time circuit is the same as that between the corresponding times on the trial circuits. When iron wire of suitable diameter, however, was substituted for copper wire of the same diameter and same geometrical form in the trial circuits, the ratio of the determinations of time in the time circuit and the ratio of the oscillations in the iron circuit were no longer constant. This inconstancy I desire to dwell upon as my strongest proof that the period of electrical oscillations on iron wires is not the same as that of oscillations on copper wires of the same geometrical form.

The arrangement of a suitable iron circuit gave me considerable trouble. The problem was to obtain a sufficient length of iron wire to show any effect of change in periodicity, and also to obtain a sufficient amount of self-induction, in order that the distances between the oscillations on the photograph should be measurable. The strong damping effect of iron did not permit of my using more than four or five metres of wire. It was not a simple matter to arrange two circuits, one of iron and one of copper, which would have exactly the same geometrical form. After many trials I arranged my trial circuit as follows :—

A cylinder of very porous wood, 11·5 centim. in diameter, 15 centim. long, was boiled in paraffin, and a spiral was cut upon its surface. The turns of the spiral were 1 centim. apart. On this cylinder and in these spirals the wires under examination were wound. After a determination had been made with a copper wire it was unwound from the cylinder and an iron or steel wire was wound in the grooves occupied by the copper wire. Exact geometrical similarity was thus obtained with good insulation. Several hundred determinations were made with wires of different sizes. With iron wires larger than ·0312 inch in diameter, no marked change in period could be perceived. If a great number, however, of photographs were measured, an inconstancy of ratios was noticed which never appeared when the copper circuits were compared. It seemed as if at certain times the iron exerted a magnetic effect and at other times failed to do this. The most marked changes in period I obtained with iron wires of ·0312 inch in diameter.



I give the following example. The lengths of the oscillations are expressed in millimetres.

IRON.		COPPER.	
A.	B.	C.	D.
Length of oscillations on iron circuit.	Length of oscillations on time circuit.	Length of oscillations on copper circuit.	Length of oscillations on time circuit.
3.7	6.08	3.50	6.14
3.7	6.08	3.40	6.00
3.7	5.90	3.30	6.00
4.0	6.10	2.70	5.26
3.3	5.16	3.40	6.10
2.8	3.60	3.37	6.36
		2.68	3.72

When the ratios of A to B and of C to D are compared, it will be seen that the time of electrical oscillations on an iron circuit of the same geometrical form as a copper circuit is longer than of those on the copper circuit.

The rate of oscillation was not far from that which I employed in my investigation on the damping effect of iron wires. Since the inductance appears under the square root in the formula  $t = \pi \sqrt{LC}$ , the changes in induction due to the iron indicated by the above table may amount to from five to ten per cent.

Thus my results confirm those of Mr. Charles E. St. John, who has shown by an entirely different method that the wavelengths sent out by a Hertzian vibrator on iron wires differ in length from those transmitted on copper wires of the same geometrical form as the iron wires. His results are of even more importance in the theory of magnetism, for they deal with more rapid electrical oscillations than those which I employed.

Jefferson Physical Laboratory.

LIV. *On the Scattering of Light by Metallic Particles.* By RICHARD THRELFALL, *Professor of Physics in the University of Sydney, N.S.W.\**

THE problem of the scattering of light by small conducting particles is treated by Prof. J. J. Thomson in his very welcome 'Recent Researches in Electricity and Magnetism.'

It would of course be absurd for me to offer any remarks on the formidable analysis by means of which Prof. Thomson reaches his conclusions; and therefore I shall limit myself to the consideration of §§ 367 and 378, in which similar conclusions are reached by different methods.

One of the most striking results is as follows ('Recent Researches,' p. 449):—"When non-polarized light falls upon a small non-conducting sphere, the scattered light will be completely polarized at any point in a plane through the centre of the sphere at right angles to the direction of the incident light. When the light is scattered by a conducting sphere, the points at which the light is completely polarized are on the surface of a cone whose axis is the direction of propagation of the incident light and whose semi-vertical angle is 120 degrees."

It may well be considered questionable whether small metallic particles can be regarded as the conducting particles to which the investigation refers, especially if we bear in mind the apparently excessive transparency of thin metallic films. However, there is no difficulty in observing the scattering from fine metallic particles; and what follows deals with some experiments I have made on the subject. To save time for any one who does not care to follow the detail of experimental work, I will state at once that I have observed no great difference in the effects produced by particles of gold, copper, iron, silver, and gum mastic. The position of the azimuth of maximum polarization with gold particles (which are most easily observed) does not differ from the corresponding position when mastic is employed by more than a degree or two, if at all. The observations with metals other than gold were nothing like so satisfactory; but so far as they go they confirm the results obtained with gold.

As long ago as 1888 I examined the properties of a gold "sky." In order that the gold particles might be suspended in a non-conducting medium, I shook up some terebene with a bit of solid phosphorus and added a very small quantity of a solution of gold chloride in ether; in the course of a few

\* Communicated by the Author.

hours, or days, the gold was thrown down as usual in particles of extreme fineness. For the present purpose, however, there is no advantage in using terebene, since any solution which is transparent must be regarded as non-conducting for voltages reversed with the frequency of light-waves. Accordingly the gold deposits which I have examined have been formed in water. When a very dilute solution of the double chloride of gold and sodium—say, one centigram of the crystallized salt per litre—is reduced by the addition of a solution of phosphorus in some organic solvent, the solution is observed, after a time varying from a few hours to several days or even weeks, to become strongly coloured. The colour varies from a clear pink with dilute solutions to an opaque purple when the solutions are strong. A number of observations on these precipitates and on their removal from suspension (for they are too fine to subside of themselves) by moulds growing in the liquids have been published by Prof. Liversidge (Australian Association for the Advancement of Science, Report, 1890). I have to thank Prof. Liversidge for allowing me to examine these solutions.

There are certain preliminary questions which must be dealt with. In the first place the precipitate formed is really gold,

- (1) Because in rather strong solutions of the chloride the precipitate forms a film on the surface which possesses the lustre of gold;
- (2) Because when the solutions are strong enough to give a precipitate coarse enough to sink, or when the fine precipitates are carried down by the growth of mould, the presence of metallic gold can be rendered evident by burnishing.

I have no formal proof that the precipitates consist of gold only; but taking into consideration the number of experiments made by Prof. Liversidge and the great variety of reducing solutions used by him, together with the constancy of the phenomena observed, there can be no doubt that the precipitate is practically pure gold. Of course, when the precipitates are large enough to examine there is no doubt about their nature, and we have no chemical reason for supposing that the reaction will change in character by the mere influence of further dilution of the solutions.

The colour of the solutions is certainly to be attributed to the presence of the precipitate; for when the precipitate is removed by moulds the colour disappears. The colour, therefore, must be due to the fine particles; but without careful examination it is difficult to believe that the whole

effect is due to scattering. This, however, appears to be most probably the case, as the following experiments will show :—

Three typical samples prepared by Prof. Liversidge were examined. The first sample had been made up about two months before I examined it. The quantity of gold was so large that the precipitate had partly subsided ; and the solution was so dark that it was practically opaque in thicknesses of more than a few centimetres. The absorption spectrum was observed with the help of a wedge-shaped bottle. The absorption was chiefly in the green and greenish blue. At about the limit of transparency practically all the spectrum disappeared except the orange-red. The opacity was such that no satisfactory observations could be made on the scattered light.

The second sample had a magnificent pink colour, very like a dilute solution of fluorescein, but of course without the fluorescence of that substance. The colour was exceedingly brilliant, and having only had experience of the colour produced by precipitates of gums in water, for a long time I imagined that some coloured substance had been formed. This specimen was described by Prof. Liversidge (*loc. cit.* p. 406). It was prepared in November 1889, and from the description of its colour cannot have changed appreciably since that date. The reducing substance was phosphorus in chloroform, and a smell of chloroform was still marked. The solution of gold chloride was of about the strength mentioned. The absorption spectrum was observed in a tube 69·3 centim. long. The absorption was not nearly so sharp as in the case of, say, chlorophyll, but was wonderfully sharp for a “sky” colour. The absorption extended from the yellow-green to the blue-green ; there also appeared to be a slight absorption in the blue ; but it was very slight. The scattered light was easily observed in this case, especially when a Nicol prism was used in conjunction with the spectroscope. It was thus discovered that the scattered light was practically green, and of about the proper apparent intensity. A line was drawn on a board so as to indicate a direction at right angles to the direction of the incident light ; and another line was drawn at 120 degrees to the same direction. By means of these lines the position for maximum polarization could be sufficiently closely observed. There can be no question as to the angle being much closer to 90°—even if it were not exactly 90°, as the observation seemed to show—than to 120°. I cannot say within what limits of angle the position was perpendicular to the direction of the incident light.

The third sample I examined had a full purple colour, and

was made at the same time as the one last described. The solution must have been of about the same strength, and the reducing agent was phosphorus dissolved in carbon bisulphide. The smell of that reagent had disappeared and been replaced by that of sulphuretted hydrogen. Observations similar to the last were made with the same general result, except that the absorption was stronger and that it extended rather further towards the red end of the spectrum. The scattered light was again seen to correspond with the part of the spectrum which was cut out in the last observation. The angle of maximum polarization occupied its former position.

A large number of similar experiments were made from time to time, but they all gave the same general results.

In order to avoid any risk of contaminating the gold with organic matter derived from the solvent used for the phosphorus, I shook up a bit of phosphorus with some distilled water, and found that I could obtain a sufficient reduction of the gold to enable me to be sure that the angle of maximum polarization occupied its former normal position.

I also set up solutions of different strengths, and observed them from day to day as the process of reduction went on; but I never observed any change in the position of the maximum angle.

Most of the observations on the direction of the position of maximum polarization were made on about a litre of the solution contained in a vessel of glass with plane sides; occasionally I used beakers, which did just as well.

The source of light was an arc lamp, and when the particles were only few and far between lenses were employed to condense the beam. Some experiments were also made with initially polarized light, but without any difference being in any case detected, whether a gold or a mastic sky was used.

#### *Metals other than Gold.*

1. *Copper*.—A solution of sulphate of copper was taken and diluted sufficiently with water that had been shaken up with phosphorus. Of course check experiments were made in this case, as in all others, to insure the absence of particles other than those desired. In many cases it was necessary to use platinum-distilled water, as ordinary once-distilled water contains too many motes. A very faint sky was obtained with the copper, and this behaved just as did the gold sky. I believe that the sky did actually consist of copper, for the solutions were both free from motes before mixing, or rather they gave a much stronger sky when mixed than when separate.

2. *Silver*.—The phosphorus-water was shaken with dilute

silver nitrate. In this case I did not succeed in satisfying myself that chlorides were sufficiently eliminated. The sky, whatever it was composed of, behaved just as before.

3. *Iron*.—A properly reduced solution of ferrous ammonium sulphate was obtained and mixed with phosphorus-water as before. The solution was more or less preserved from oxidation by covering it with a layer of "albolene" oil. I am not sure that an appreciable increase of the sky took place on this occasion by the action of the phosphorus: what sky there was behaved as before.

The above experiments were repeated, a piece of phosphorus being left in the liquid; but though the skies became rather stronger, no differences could be detected. These experiments suffer from the uncertainty that the skies might have been formed by particles separated direct from the phosphorus.

Assuming that Prof. Thomson's views are correct, these experiments must, I think, be taken as showing that at all events gold in particles fine enough to scatter light behaves as an insulator. At all events, the phenomena are consistent with the great transparency of gold-leaf.

No difference was observed between the scattering of plane waves, and the scattering from a pencil of rays converging from the condenser of the lantern.

Returning to the gold solutions, I have no hesitation in saying that they afford the simplest and most beautiful illustration of the colours produced by fine particles. It is worthy of note that the colours are so brilliant, even if we allow for the manner in which the colour of the scattered light depends on the size of the particles.

The apparent perfect transparency of the more dilute solutions, when considered in connexion with the comparative sharpness of the absorption spectrum, must indicate a uniformity in the dimensions of the particles which is, so far as I know, unique.

Judging from the appearance of the spectrum only, especially in the case of the stronger solutions—*i. e.*, those that just do not settle by themselves—I think that perhaps an excellent light for photographic purposes might be obtained by using these skies as light-filters.

### *Supplementary Note.*

After concluding the above experiments it appeared to me that the only metal for which the evidence I had to offer was satisfactory was gold. I therefore made the following experiments with the object of observing the action of a "sky"

of platinum particles. Platinum is certainly one of the most opaque, if not the most opaque metal ordinarily dealt with ; and it seemed possible that very fine particles of platinum might act as conductors even to electric disturbances reversed with the frequency of blue light.

A sky of platinum particles was easily produced as follows:—A litre bottle with a wide neck was three quarters filled with boiling distilled water, the water having boiled for an hour before being poured into the bottle. The rubber bung used to close the bottle was pierced by three holes—one allowing the introduction of a thick glass tube carrying a sealed-in electrode and passing into the water ; another carried a second electrode of platinum reaching down to within about half an inch of the water surface ; the third carried a tube permitting communication to be made between the inside of the bottle and the water-pump. On placing the bung in position and working the pump, most of the air was rapidly sucked from the bottle, the water began to boil, and after a time the connexion was sealed-off. The bung and tubes were well waxed, and the bottle was left to cool down. Next day it was found that the water “hammered” in a satisfactory manner when the bottle was shaken. The electrode, owing to several causes, was now about  $1\frac{1}{2}$  centim. from the surface of the water. An induction-coil worked by a transformer was then caused to pass a current between the water surface and the free electrode, the current being regulated so that at a frequency of about 60 ~ it just failed to produce sufficient electrolysis to free gas. The electrode was white hot. The bottle was placed before an arc-lamp and studied by a Nicol prism, as previously described, while the coil was actually at work. It was noted that before the discharge began the water was nearly optically clean, and looked exactly like a check-sample of the boiled distilled water which had been preserved for the purpose of comparison. After about half an hour’s discharge no appreciable increase in the scattered light could be detected ; but on shaking the bottle, small brightly-reflecting metallic scales became apparent. The discharge produces considerable motion of the water-surface, and it had been erroneously assumed that this would prevent the formation of a platinum film on the water surface. The hint was taken, however, and the bottle was shaken by hand for about two hours while the discharge was taking place, during the whole of which time the scattering of light by the water particles continually increased, and was finally fairly brilliant. At no time did the direction of maximum polarization appear to vary from the perpendicular to the direction of propagation

of the light. The platinum sky behaved, in fact, in a quite normal manner. The more carefully the directions of the incident and observed light were adjusted to perpendicularity, the more complete the extinction produced by rotating the Nicol appeared to be. The fine particles remaining well suspended for a considerable time (at least a week), several friends were good enough to examine the polarization phenomena for me, and all the observations agreed perfectly.

Platinum particles therefore scatter light like ordinary non-conducting particles within the limits of accuracy of the observations.

I was anxious to try the effect of a sky of iron particles, and made the following experiments and observations on this matter.

The apparatus used was similar to that described in the case of platinum, except that "pure" iron electrodes were formed by binding the iron wire sold as "pure for chemical analysis" round the sealed-in ends of the platinum wires. Five or six layers of fine iron wire were bound round the platinum wire, and connected then to the actual electrodes—two short lengths of Swedish charcoal-iron carefully cleaned. Sparks were taken between the two electrodes, and were practically confined in their effects to the charcoal-iron. As a medium for catching and supporting the fine iron-dust, I first tried a nearly dry sample of glycerine, prepared by heating the strongest commercial glycerine in the presence of strong sulphuric acid under reduced pressure. After sparking for some hours a sky was formed, but the heat of the discharge had been sufficient to obviously decompose some glycerine vapour, and consequently the sky might have been due to iron, oxide of iron, or carbon, or any mixture thereof. I therefore tried to find some more suitable substance than glycerine. I wished to exclude oxygen, if possible, from the medium employed, and yet have a substance which should have only a small vapour-tension. After a good many trials I settled on a vaseline oil (?) known as "albocarbene oil." The vapour-tension of this substance was at least 2 centim. at  $24^{\circ}$  C. even after heating and exposing in a vacuum several times. Under the circumstances it hardly appeared worth while to attempt to take up the oxygen it might hold by the action of sodium, especially as I was not sure of the complete action of the sodium; while the certainty of its making the oil dirty opened up the probability of other disadvantages. The atmosphere employed was hydrogen disengaged from zinc and hydrochloric acid in presence of chromous chloride; it was washed by solution of sodium hydrate, and finally dried



over phosphorus pentoxide. The pressure was about two inches of mercury. The sparking &c. was carried out as before, and after about four hours' of sparking a fairly good sky was visible in spite of the strong fluorescence of the oil. On opening the bottle a decided smell of hydrocyanic acid was noted (nitrogen was known to be present in small quantities), and there were traces of decomposition on the sides of the bottle. An attempt was made to concentrate the particles by standing the bottles on the poles of a Jamin magnet, but no concentration could be observed after twenty-four hours. Considering the viscosity of the oil, this was not regarded as of much weight. The oil was then poured through a filter made from Schleicher and Schull's special quality paper for stopping fine particles. The paper was washed with kerosene, gasoline, alcohol, and water, and was finally digested in dilute hydrochloric acid. The resultant liquid, on evaporation, showed the presence of traces of iron in an unmistakable manner. The filtered oil was not examined as to its scattering properties, owing to an accident.

The light scattered from the supposed iron sky behaved in a perfectly normal manner, *i. e.* like all substances hitherto examined. In this case it was found more convenient to use a beam of sunlight than the light from the arc-lamp; observations are rendered difficult by the blue fluorescence of the oil. The question turns entirely on the point as to whether the scattering was produced by metallic iron or by its oxide. That the scattering was produced by one or the other I have no doubt; for after filtering the oil I could discern a faint darkening of the filter-paper which disappeared by treatment with hydrochloric acid, and so disposes of the supposition that the particles were carbon. The iron afterwards found was from the deposit and not originally in the acid or reagents, or in the filter-paper (for check-experiments were made). Some dust on the electrode appeared to be magnetic when tested by a magnetized sewing-needle, but the quantity that I could collect was too small to make the observation conclusive. Of course if I had been in a position to secure a sample of a definite hydrocarbon of small vapour-tension, the matter could easily have been determined; but such a thing does not exist, to my knowledge, in Australia.

As I desired further evidence I repeated the whole investigation up to the sparking, but this time introduced a small plate of glass between the oil and the electrodes. After sparking as before for three hours (using the coil-contact and three gallon leyden jars with an air-gap) I could see no mirror, though obviously a good deal of oil-vapour had been

decomposed. (Professor Wright, of Yale, warned me in 1889 that iron mirrors are not easily made.) The experiment was perforce interrupted for three days, and on turning on the coil on the fourth day a smart explosion resulted, bringing the observations to a conclusion by scattering every part of the apparatus, the writer having a rather lucky escape. The electrodes were picked up and found to be perfectly clean and bright. After consideration I decided not to pursue the matter further, first because I am not quite sure of the importance of an investigation of iron in the present state of electromagnetic theory, and secondly because the investigation can be easily made by anyone who has a suitable hydrocarbon, whereas I can only hope to obtain inconclusive results with the oils at my disposal.

I will add a note on producing oxygen-free atmospheres. If hydrogen is employed the difficulty is to get rid of oxygen from the water and acid used to act upon the zinc. Several ways of absorbing small quantities of oxygen are known and dealt with in a paper by me, "On the Preparation of Pure Nitrogen and Attempts to Condense it," *Phil. Mag.* January 1893.

The most convenient way of obtaining large quantities of hydrogen free from oxygen is to half fill a very large flask with granulated zinc and keep this covered with a solution of chromous chloride—the "liquide brute" of Recoura. Hydrochloric acid can be added fearlessly by means of an ordinary safety funnel; for any air carried down is instantly deprived of its oxygen by the blue liquid. If the flask be permanently sealed to a potash wash-bottle and drying-tubes, a means of procuring dry hydrogen with traces of nitrogen is instantly and continually available. The blue liquid does not last for ever, however, though if a little acid be added from time to time its life is sufficiently prolonged. Following Recoura in the paper quoted, I recommended that the potassium dichromate should be finely ground in the chromous chloride preparation. I now find that if it is dissolved in the hydrochloric acid before the latter is added to the zinc, it does just as well and saves a good deal of trouble.

To sum up :—

1. The scattered light from gold and platinum particles behaves like light scattered from particles of gum mastic or milk so far as the polarization phenomena are concerned.

2. The same remark applies to iron, or iron oxide, or carbide, whichever it was that I examined. I rather think, on the whole, that the sky was iron simply.

*Note on the preceding Paper by Prof. J. J. THOMSON.*

I made, about two years ago, some rough experiments on the polarization of light scattered by small particles of gold, the results of which were in agreement with those of Professor Threlfall. I regarded these experiments as confirming the results of Maxwell and Wien, that the resistance of metals to the very rapidly alternating currents which constitute light is much greater than to steady currents.

It is, moreover, difficult to make these experiments so as to be a fair test of the theory, as it is only when the size of the particles is within narrow limits that the theory would be applicable, even supposing the resistance to be as low as for steady currents. To scatter the light the diameters of the particles must be small compared with the wave-length of light, while the theory given in my 'Researches on Electricity and Magnetism' requires that the depth to which the currents produced by the light penetrate the particle should be a small fraction of the radius of the particle. Now at a depth  $d$  below the surface of the sphere the intensity of the induced current varies as  $e^{-kd}$ , where  $k = \{2\pi\mu p/\sigma\}^{\frac{1}{2}}$ , where  $\mu$  is the magnetic permeability,  $\sigma$  the specific resistance of the metal, and  $2\pi/p$  the time of oscillation of the incident electrical vibration. Thus the currents at a depth  $1/k$  below the surface will only be  $1/e$  of their value at the surface; we may therefore take  $1/k$  as the measure of the thickness of the film filled by the currents. For gold  $\sigma = 2100$  for steady currents,  $\mu = 1$ , and for the D line  $p = 2\pi \times 5.097 \times 10^{14}$ ; thus  $1/k = 3.2 \times 10^{-7}$ . The wave-length of the D line is  $5.89 \times 10^{-5}$ , about 170 times  $1/k$ . Thus, for the theory to be applicable, the diameter of the particles must be small compared with  $\lambda$  and large compared with  $1/k$ . As  $\lambda$  is only 170 times  $1/k$  this makes the range for the diameter very small. A more satisfactory test of the theory could be made with longer wave-lengths and larger particles; for the thickness to which the currents descend varies as the square root of the wave-length, so that the ratio of the wave-length to the thickness of the current-film increases as the wave-length increases.

LV. *On the Self-Induction and on the Gravity-Potential of a Ring.* By W. M. HICKS\*.

THE self-induction of a finite ring has been considered by Professor Minchin in the March number of the *Philosophical Magazine* on the assumption that it is the flux through a diaphragm composed of the aperture and half the surface of the ring. In reading this paper it occurred to me that the problem could more naturally be attacked by means of Toroidal Functions. In considering it from this point of view I was led to a conclusion which does not seem to have been heretofore noticed.

The expression for the self-induction of a thin circular ring as given by Maxwell is  $\pi R(4 \log 8R/r - 8)$ , and for a ring of finite size as given by Minchin is  $\pi R(4 \log 8R/r - 8)$  + terms involving the radius ( $r$ ) of the transverse section. In the finite ring the current-density varies inversely as the distance from the straight† axis. In Maxwell's wire the distribution of current across the transverse section is considered uniform, and it would therefore appear that his formula gives the self-induction so far as it is independent of the thickness, and that this part is independent of the distribution of current-density within the wire itself. As a matter of fact, however, the distribution of current-density has a deciding effect on the value of the second term, and this however small the section of the ring may be. The correct value of the self-induction, neglecting powers of  $r/R$ , is  $\pi R(4 \log 8R/r - 7)$ . The expression  $\pi R(4 \log 8R/r - 8)$  gives the value of the flux through the *aperture* only, which to this degree of approximation is independent of the law of current-density. The difference is due to the fact that although the section across the ring may be exceedingly small, yet the forces are correspondingly large, and the interaction of the different parts of the current cannot be neglected even when the ring is extremely thin and of large aperture. *E. g.* in a ring of 1 metre radius and 1 millim. thick the usually accepted formula gives a value  $3\frac{1}{2}$  per cent. too small.

In the present paper the question is treated by the method usually employed in dealing with problems of electric potential and fluid motion, but which, so far as I know, is new in its application to electromagnetic and gravity potentials. The

\* Communicated by the Author.

† By *straight* axis is meant the line through the centre of the ring perpendicular to its plane. The *circular* axis is the locus of the centres of the transverse sections of the ring.

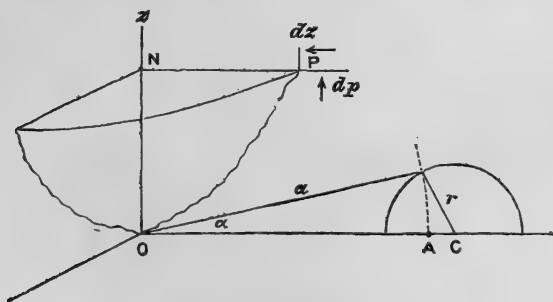
functions which naturally come in are Toroidal Functions, the properties of which are developed in two papers in the Transactions of the Royal Society\*. These papers are referred to in the present pages as [T. F. i.] and [T. F. ii.].

The special problems considered are:—

- (1) The force-flux function and self-induction for a ring in which the current-density varies inversely as the distance from the straight axis. This is the case of current through a ring consisting of a single turn of round wire.
- (2) The same quantities when the current-density is constant. This leads to the case of a uniformly wound coil of circular cross section.
- (3) The method is then exemplified by finding the gravity-potential of a finite ring—a problem which has been recently very fully considered by Mr. Dyson†.

1. The force is symmetrical round the straight axis of the ring. Take this axis for the axis of  $z$  and the origin at the centre of the ring, and let  $\rho, z$  denote the cylindrical coordinates of any point. Further, let  $R$  denote the radius of the circular axis,  $r$  that of a cross section, and  $a$  that of the critical circle in the curvilinear coordinates used in toroidal functions—*i. e.* in the system of coaxial circles having  $Oz$  for common radical axis and having one circle of the system coinciding with the cross section. The length of  $a$  is equal to the length of a tangent line from the centre to the circle. It will be found convenient to express values later in terms of  $R$  and the angle subtended at the centre by a cross section: this angle will be denoted by  $\alpha$ .

The flux function  $\psi$  at a point  $P$  will be taken as denoting



the total flux  $\psi$  through a circle, radius  $PN$  (see figure). It is the same as that through a diaphragm stretching from  $O$

\* Phil. Trans. 1881, Part iii. p. 609, and 1884, Part i. p. 161.

† Phil. Trans. 1893, A. pp. 43 & 1041.

and bounded by this circle. Let  $w, w'$  denote the velocities at P parallel to NP and Oz. Then

$$\frac{d\psi}{d\rho} d\rho = \text{flux up through an annulus whose radii are PN and PN} + d\rho,$$

$$= 2\pi\rho d\rho w',$$

$$\frac{d\psi}{dz} dz = \text{flux through cylindrical tyre (breadth } dz) \text{ towards N,}$$

$$= -2\pi\rho dz w;$$

whence

$$w = -\frac{1}{2\pi\rho} \frac{d\psi}{dz}, \quad w' = \frac{1}{2\pi\rho} \frac{d\psi}{d\rho}.$$

2. Consider a current flowing through an elementary ring whose cross section is  $d\rho dz$  and in which the current-density is  $\sigma$ . Then the circulation taken round this

$$= 4\pi \times \text{current} = 4\pi\sigma d\rho dz.$$

But the circulation

$$= \left( \frac{dw}{dz} - \frac{dw'}{d\rho} \right) d\rho dz = 4\pi\sigma d\rho dz;$$

whence

$$\frac{1}{2\pi\rho} \frac{d^2\psi}{dz^2} + \frac{d}{d\rho} \left( \frac{1}{2\pi\rho} \frac{d\psi}{d\rho} \right) = -4\pi\sigma,$$

or

$$\frac{d^2\psi}{dz^2} + \frac{d^2\psi}{d\rho^2} - \frac{1}{\rho} \frac{d\psi}{d\rho} = -8\pi^2\rho\sigma. \quad \dots \quad (1)$$

At points where there is no current the right-hand side is of course zero.

3. To find the force-flux we shall require two functions, one ( $\psi'$ ) for space outside the ring, and the other ( $\psi$ ) for space inside. The conditions which they have to fulfil are as follows:—

$\psi'$  must be finite at all points outside the ring, be zero at the point O, and satisfy the equation

$$\frac{d^2\psi'}{dz^2} + \frac{d^2\psi'}{d\rho^2} - \frac{1}{\rho} \frac{d\psi'}{d\rho} = 0.$$

Using toroidal functions, these conditions are satisfied by

$$\psi' = \frac{1}{\sqrt{(C-c)}} \sum R_n (A_n \cos nv + A'_n \sin nv).$$

$\psi$  must be finite at all points inside the ring, and must satisfy

$$\frac{d^2\psi}{dz^2} + \frac{d^2\psi}{d\rho^2} - \frac{1}{\rho} \frac{d\psi}{d\rho} = -8\pi^2\rho\sigma. \quad (1)$$

These conditions are satisfied by

$$\psi = f + \frac{1}{\sqrt{(C-c)}} \Sigma T_n (B_n \cos nv + B'_n \sin nv),$$

where  $f$  is any particular solution of the equation (1).

Further, at the boundary of the ring  $\psi$  and the force are continuous. That is, when  $u = u_0$  then for all values of  $v$ ,

$$\psi = \psi' \quad \text{and} \quad \frac{d\psi}{du} = \frac{d\psi'}{du}, \quad (2)$$

where  $u_0$  is the value of  $u$  corresponding to the boundary. These conditions will serve to find completely  $\psi$  and  $\psi'$  in all cases.

In order to apply these last conditions it will be necessary to expand  $f$  in a series of cosines and sines of multiple angles. In the cases here considered it will be seen later that the sine terms do not enter, and that  $f$  is of the form

$$f = \frac{1}{\sqrt{(C-c)}} \Sigma F_n \cos nv,$$

where  $F_n$  is a function of  $u$  only.

The conditions (2) now give

$$A'_n = 0, \quad B'_n = 0.$$

$$A_n R_n = B_n T_n + F_n,$$

$$A_n R'_n = B_n T'_n + F'_n;$$

where dashed letters denote differentiation with respect to  $u$ , and the functions are now to be regarded as *functions of  $u_0$  only*.

From these,

$$A_n (R'_n T_n - R_n T'_n) = T_n F'_n - T'_n F_n,$$

$$B_n (R'_n T_n - R_n T'_n) = R_n F'_n - R'_n F_n.$$

Now

$$R'_n T_n - R_n T'_n = (n^2 - \frac{1}{4}) S^2 (P'_n Q_n - P_n Q'_n) \quad [\text{T. F. ii. 2.}]$$

$$= (n^2 - \frac{1}{4}) \pi S. \quad [\text{T. F. i. 24.}]$$

Hence

$$\left. \begin{aligned} A_n &= \frac{4}{(4n^2-1)\pi S} (T_n F'_n - T'_n F_n), \\ B_n &= \frac{4}{(4n^2-1)\pi S} (R_n F'_n - R'_n F_n). \end{aligned} \right\} \quad \dots \quad (3)$$

This is the general solution for any case in terms of  $F$ .

4. We proceed to apply the foregoing to special cases. Consider, first, the case of a current flowing in a uniform circular ring of any size. The parts of the current all flow in circles, and the equipotential surfaces will be planes through the straight axis. The lengths of conductor which a current uses between two such surfaces will be proportional to the arc between—i. e., to  $\rho$ . Hence, in order that each element of current may produce equal fall of potential between the two planes, the current-density must vary inversely as  $\rho$ , i. e.  $\sigma = b/\rho$ , where  $b$  is some constant. Let  $I$  denote the total current; then, integrating over a cross section, it will be found that

$$I = 2\pi b \{R - \sqrt{(R^2 - r^2)}\}.$$

$$\text{Now} \quad r = R \sin \alpha, \quad a = R \cos \alpha; \quad \dots \quad (4)$$

$$\text{whence} \quad I = 2\pi b R (1 - \cos \alpha),$$

$$\text{or} \quad \sigma = \frac{I}{2\pi \rho R (1 - \cos \alpha)}. \quad \dots \quad (5)$$

Equation (1) now becomes

$$\frac{d^2 \psi}{dz^2} + \frac{d^2 \psi}{d\rho^2} - \frac{1}{\rho} \frac{d\psi}{d\rho} = -8\pi^2 b,$$

a particular solution of which is

$$\begin{aligned} f &= -4\pi^2 b z^2 \\ &= -4\pi^2 b a^2 \frac{\sin^2 v}{(C-c)^2} \quad [\text{T. F. i. 3}]. \end{aligned}$$

This has to be expanded in a series of the form

$$-4\pi^2 b a^2 \frac{\sin^2 v}{(C-c)^2} = \frac{1}{\sqrt{(C-c)}} \Sigma F_n \cos nv.$$

It is clear that there are no terms in  $\sin nv$ . Hence

$$\begin{aligned} \frac{\pi}{2} F_n &= -4\pi^2 b a^2 \int_0^\pi \frac{\sin^2 v \cos nv}{(C-c)^{\frac{3}{2}}} dv \\ &= \frac{4\pi^2 b a^2}{S} \frac{d}{du} \int_0^\pi \frac{\cos nv - \frac{1}{2}(\cos \overline{n+2v} + \cos \overline{n-2v})}{\sqrt{(C-c)}} dv \\ &= \frac{4\pi^2 b a^2 \sqrt{2}}{S} \frac{d}{du} \{Q_n - \frac{1}{2}(Q_{n+2} + Q_{n-2})\} \quad [\text{T. F. ii. 1}]; \end{aligned}$$



therefore

$$F_n = \frac{4\pi b a^2 \sqrt{2}}{S} \{ (Q'_n - Q'_{n-2}) - (Q'_{n+2} - Q'_n) \} \\ = 8\pi b a^2 \sqrt{2} \{ (n-1) Q_{n-1} - (n+1) Q_{n+1} \};$$

also

$$F_0 = -8\pi b a^2 \sqrt{2} Q_1.$$

It is now only necessary to substitute these values in equations (3). Then

$$T_n F'_n - T'_n F_n = 8\pi b a^2 \sqrt{2} [ -S Q'_n \{ (n-1) Q'_{n-1} - (n+1) Q'_{n+1} \} \\ + (n^2 - \frac{1}{4}) S Q_n \{ (n-1) Q_{n-1} - (n+1) Q_{n+1} \} ];$$

since

$$T_n = -S Q'_n \text{ and } T'_n = -(n^2 - \frac{1}{4}) S Q_n.$$

Now

$$(n^2 - \frac{1}{4}) Q_n Q_{n-1} - Q'_n Q'_{n-1} \\ = \frac{2n+1}{4} Q_n \{ 4n C Q_n - (2n+1) Q_{n+1} \} - Q'_n (Q'_{n+1} - 2n S Q_n);$$

since

$$(2n+1) Q_{n+1} - 4n C Q_n + (2n-1) Q_{n-1} = 0$$

and

$$Q'_{n+1} - Q'_{n-1} = 2n S Q_n.$$

Therefore

$$\left( n^2 - \frac{1}{4} \right) Q_n Q_{n-1} - Q'_n Q'_{n-1} \\ = - \frac{(2n+1)^2}{4} Q_n Q_{n+1} - Q'_n Q'_{n+1} + n Q_n \{ (2n+1) C Q_n + 2 S Q'_n \} \\ = \left\{ n(2n+1) - \frac{(2n+1)^2}{4} \right\} Q_n Q_{n+1} - Q'_n Q'_{n+1} \\ = \left( n^2 - \frac{1}{4} \right) Q_n Q_{n+1} - Q'_n Q'_{n+1};$$

therefore

$$T_n F'_n - T'_n F_n = -16\pi b a^2 \sqrt{2} \left\{ \left( n^2 - \frac{1}{4} \right) Q_n Q_{n+1} - Q'_n Q'_{n+1} \right\};$$

whence

$$A_n = - \frac{16\pi b a^2 \sqrt{2}}{n^2 - \frac{1}{4}} \left\{ \left( n^2 - \frac{1}{4} \right) Q_n Q_{n+1} - Q'_n Q'_{n+1} \right\} \\ = 16\pi b a^2 \sqrt{2} \alpha_n \text{ (say)} \quad (6)$$

with

$$A_0 = -8\pi b a^2 \sqrt{2} (Q_0 Q_1 + 4 Q'_0 Q'_1).$$

If  $(n^2 - \frac{1}{4})Q_n Q_{n+1} - Q'_n Q'_{n+1}$  be written  $X_n$ , it can be shown that

$$X_n = X_{n-1} + (2n-1)Q_n Q_{n-1},$$

which is more convenient for calculation.

So also

$$R_n F'_n - R'_n F_n = 8\pi b a^2 \sqrt{2} [S P'_n \{ (n-1)Q'_{n-1} - (n+1)Q'_{n+1} \} \\ - (n^2 - \frac{1}{4}) S P_n \{ (n-1)Q_{n-1} - (n+1)Q_{n+1} \}].$$

As in the former case, it may be shown that

$$(n^2 - \frac{1}{4})P_n Q_{n-1} - P'_n Q'_{n-1} = 2n\pi + (n^2 - \frac{1}{4})P_n Q_{n+1} - P'_n Q'_{n+1},$$

and

$$B_n = \frac{-16ba^2 \sqrt{2}}{n^2 - \frac{1}{4}} \left\{ n(n-1)\pi - \left( n^2 - \frac{1}{4} \right) P_n Q_{n+1} + P'_n Q'_{n+1} \right\} \\ = 16ba^2 \sqrt{2} \beta_n \text{ (say)}$$

with

$$B_0 = 8ba^2 \sqrt{2} (P_0 Q_1 + 4P'_0 Q'_1).$$

Also, if the expression in the bracket for  $B_n$  be denoted by  $Y_n$ ,

$$Y_n = Y_{n-1} + 2(n-1)\pi + (2n-1)P_{n-1}Q_n.$$

Thus  $\psi$  and  $\psi'$  are now completely determined. It must be remembered that the functions  $P$ ,  $Q$  in formulæ (6) and (7) are the values at the surface of the tore  $u_0$ .

5. In dealing with the self-induction of such a ring as we are now considering, it is necessary to particularize. Its value will differ for alternating currents of different periods. The time-constant for a constant E.M.F. applied to the ring will not be the same as on the assumption here made as to distribution of current-density. In order to be definite we will find the coefficient for the energy on the assumption of steady current—in other words, the value of  $L$  in the expression  $\frac{1}{2}LI^2$ . This will very approximately give the self-induction except for rapid alternations. The energy is given by

$$E = \frac{1}{2} \iint \psi \sigma \, d\rho \, dz,$$

the integral being taken over a cross section.

Putting in the value of  $\psi$  and transferring to curvilinear coordinates,

$$E = -2\pi^2 b^2 \iint \frac{z^2}{\rho} \, d\rho \, dz + \frac{1}{2} b \Sigma \iint \frac{B_n T_n \cos nv}{\sqrt{(C-c)}} \cdot \frac{1}{\rho} \frac{dn}{du} \cdot \frac{dn'}{dv} \, du \, dv \\ = -\frac{2}{3} \pi^3 b^2 R^2 (1 - \cos \alpha)^2 (1 + 2 \cos \alpha) + ab \Sigma B_n \int_{u_0}^{\infty} \int_0^{\pi} \frac{T_n \cos nv}{S(C-c)^{\frac{3}{2}}} \, dv \, du$$

Now

$$\int_0^{\pi} \frac{\cos nv}{(C-c)^{\frac{3}{2}}} \, dv = -\frac{2\sqrt{2}}{S} Q'_n;$$

therefore

$$E = -\frac{2}{3}\pi^3 b^2 R^2 (1 - \cos \alpha)^2 (1 + 2 \cos \alpha) + 2\sqrt{2ab}\Sigma B_n \int_{u_0}^{\infty} \frac{1}{S} (Q'_n)^2 du.$$

The integral may be evaluated as follows :

$$Q'_{n+1} - Q'_{n-1} = 2n S Q_n.$$

Also it may easily be proved that

$$Q'_{n+1} + Q'_{n-1} = 2C Q'_n + S Q_n;$$

Therefore

$$(Q'_{n+1})^2 - (Q'_{n-1})^2 = 2nS(2C Q'_n Q'_n + S Q_n^2)$$

$$= 2nS \frac{d}{du} (C Q_n^2);$$

therefore

$$\int_{u_0}^{\infty} \frac{1}{S} (Q'_{n+1})^2 du - \int_{u_0}^{\infty} \frac{1}{S} (Q'_{n-1})^2 du = [2n C Q_n^2]_{u_0}^{\infty} \\ = -2n C Q_n^2,$$

or, say,

$$X_{n+1} - X_{n-1} = -2n C Q_n^2;$$

therefore

$$X_n = 2C \{ (n+1) Q_{n+1}^2 + (n+3) Q_{n+3}^2 + \dots \},$$

an infinite and rapidly convergent series.

Substituting this and the value of  $b$  from (5),

$$E = -\frac{\pi R I^2}{6} (1 + 2 \cos \alpha) + \frac{R \sqrt{2}}{2} \cdot \frac{I^2 \cos \alpha}{(1 - \cos \alpha)^2} \Sigma \frac{B_n X_n}{\pi^2 R^2 b},$$

and the self-induction,

$$= -\frac{\pi R}{3} (1 + 2 \cos \alpha) + 32 \pi R \cdot \frac{\cos^3 \alpha}{(1 - \cos \alpha)^2} \Sigma \frac{\beta_n X_n}{\pi^3}. \quad (8)$$

Now

$$P_n = \alpha_n E' + \beta_n F',$$

$$Q_n = \alpha_n (F - E) + \beta_n F,$$

where  $E, F$  are elliptic integrals to modulus  $k$ ; where

$$k^2 = \frac{1 - \cos \alpha}{1 + \cos \alpha},$$

$E', F'$  are the complementary integrals.

Also  $\alpha_n, \beta_n$  are algebraical expressions in  $k$  whose values are given up to  $n=5$  in [T. F. ii. 8]. Their general values are also given in a paper by Mr. Basset\*. Consequently the

\* "On Toroidal Functions," Amer. Journ. Math. xv. p. 301.

flux functions (and therefore forces) and self-induction of large toroids of any size may be calculated to any desired degree of approximation directly from the formulæ obtained. When, however, the rings are of smaller cross section, and  $k$  small, it is more convenient to have the formulæ expressed directly in terms of  $k$ .

6. Putting in the values of  $P$ ,  $Q$  given in [T. F. ii. 9, 10], and remembering that  $d/du = -kd/dk$ , it will be found that,  $L$  denoting  $\log_e 4/k$ ,

$$\frac{\beta_0}{\pi} = \frac{1}{2}k^2 \left\{ 4L - 6 + \left( 7L - \frac{43}{4} \right) k^2 + \left( \frac{81}{8}L - \frac{489}{32} \right) k^4 \right\},$$

$$\frac{\beta_1}{\pi} = 2k^2 \left\{ 1 - \left( \frac{3}{4}L - \frac{13}{8} \right) k^2 \right\},$$

$$\frac{\beta_2}{\pi} = -\frac{8}{15} \left( 1 - \frac{15}{8}k^2 \right),$$

$$\frac{\beta_3}{\pi} = -\frac{24}{35};$$

and that the self-induction

$$\begin{aligned} &= -\frac{\pi R}{3} (1 + 2 \cos \alpha) + \frac{4\pi R \cos^3 \alpha}{(1 + \cos \alpha)^2} \left\{ 4L - 6 + (14L - 18)k^2 \right\} \\ &= \pi R \left[ \frac{4 \cos^3 \alpha}{(1 + \cos \alpha)^2} \left\{ 4L - 6 + (14L - 18)k^2 \right\} - \frac{1 + 2 \cos \alpha}{3} \right]; \end{aligned}$$

when  $\alpha$  is very small this is  $\pi R(4L - 7)$ , and not  $\pi R(4L - 8)$  as usually assumed.

Taking Professor Minchin's example,  $R = 1$  cm.,  $r = \cdot 1$  cm.,

$$\sin \alpha = \cdot 1, \quad \cos \alpha = \cdot 995, \quad k^2 = 10025,$$

and self-induction = 33·36 C.G.S. units. The formula  $4\pi R(L - 2)$  gives 29·9. The numerical values given by Prof. Minchin appear to be doubled, as if he had used the diameter instead of the radius.

Similarly,

$$\alpha_0 = -\pi^2 k^2 \left( 1 + \frac{7}{4}k^2 + \frac{81}{32}k^4 \right),$$

$$\alpha_1 = \frac{3}{4}\pi^2 k^4 \left( 1 + \frac{11}{6}k^2 \right),$$

$$\alpha_2 = \frac{5}{32}\pi^2 k^6.$$

Hence, for space outside the ring,

$$\begin{aligned}\psi &= \frac{16\pi^2 a^2 b \sqrt{2k^2}}{\sqrt{(C-c)}} \left\{ -\left(1 + \frac{7}{4}k^2 + \frac{81}{32}k^4\right)R_0 \right. \\ &\quad + \frac{3}{4}k^2\left(1 + \frac{11}{6}k^2\right)R_1 \cos v \\ &\quad \left. + \frac{5}{32}k^4 R_2 \cos 2v + \dots \right\} \\ &= \frac{8\pi R I \sqrt{2} \cos^2 \alpha}{1 + \cos \alpha} \frac{1}{\sqrt{(C-c)}} \left\{ \&c. \right\}.\end{aligned}$$

The total flux through the aperture is the value of  $\psi$  at the inside edge, *i. e.* at  $u=u_0$ ,  $v=\pi$ .

Then

$$\begin{aligned}\psi &= \frac{16\pi R I \cos^2 \alpha}{1 + \cos \alpha} \frac{\sqrt{k}}{1+k} \left\{ -\left(1 + \frac{7}{4}k^2 + \frac{81}{32}k^4\right)R_0 \right. \\ &\quad - \frac{3}{4}k^2\left(1 + \frac{11}{6}k^2\right)R_1 \\ &\quad \left. + \frac{5}{32}k^4 R_2 \right\}.\end{aligned}$$

Substituting for the R it will be found that

$$\begin{aligned}\psi/I &= \frac{8\pi R \cos^2 \alpha}{(1 + \cos \alpha)(1+k)} \left\{ L - 2 - \frac{3}{4}k + \frac{1}{2}\left(L + \frac{1}{8}\right)k^2 + \frac{3}{8}\left(3L - \frac{31}{6}\right)k^3 \right\}, \\ \text{which for very small rings gives the self-induction} \\ &= 4\pi R(L-2),\end{aligned}$$

the value usually accepted for the true value.

The flux as taken by Prof. Minchin is found by putting  $v=0$ , when

$$\psi/I = \frac{8\pi R \cos^2 \alpha}{(1 + \cos \alpha)(1-k)} \left\{ L - 2 + \frac{3}{4}k + 2\left(L - \frac{23}{32}\right)k^2 - \frac{3}{8}\left(3L - \frac{31}{6}\right)k^3 \right\}.$$

This agrees with his result up to the term in  $k$ .

The force at the centre of the ring is

$$\frac{1}{2\pi\rho} \frac{d\psi}{du} \cdot \frac{du}{dn} \quad \text{when } u=0 \text{ and } v=\pi.$$

This

$$\begin{aligned}&= \frac{1}{2\pi S} \left(\frac{C-c}{a}\right)^2 \left[ -\frac{S\psi}{2(C-c)} + \frac{1}{\sqrt{(C-c)}} \Sigma \left(n^2 - \frac{1}{4}\right) A_n S P_n \cos nv \right] \\ &= \frac{2^{\frac{3}{2}}}{2\pi a^2} \pi \Sigma (-1)^n \left(n^2 - \frac{1}{4}\right) A_n \\ &= 32b \left\{ \frac{1}{2} (Q_0 Q_1 + 4 Q'_0 Q'_1) + \Sigma_1 (-1)^n \left(Q'_n Q'_{n+1} - \overline{n^2 - \frac{1}{4}} Q_n Q_{n+1}\right) \right\}.\end{aligned}$$

When small this becomes

$$= \frac{2\pi I}{R} \left( 1 + \frac{1}{2} k^2 + \frac{1}{4} k^4 \right).$$

7. The case of uniform current-density is of more practical importance, as it leads to the case of a uniformly-wound circular coil whose cross section is also circular. The mathematical treatment, however, does not lead to such a complete solution as in the former case.

As the current-density is uniform,  $\sigma = I/\pi r^2$ , and the right-hand side of equation (1) is  $-8\pi I\rho/r^2$ .

A particular integral is

$$f = -\frac{8}{3}\pi \frac{I}{r^2} \cdot \rho^3 = -\frac{1}{\sqrt{(C-c)}} \times \frac{8\pi I\alpha^3 S^3}{3r^2(C-c)^{\frac{5}{2}}},$$

whence

$$F_n = -\frac{16 I\alpha^3 S^3}{3r^2} \int_0^\pi \frac{\cos nv}{(C-c)^{\frac{5}{2}}} dv.$$

Now

$$Q_n \sqrt{2} = \int_0^\pi \frac{\cos nv}{(C-c)^{\frac{3}{2}}} dv;$$

whence it is easy to show that

$$\left. \begin{aligned} F_n &= -\frac{64\sqrt{2}I\alpha^3}{9r^2} (SQ_n'' - CQ_n'), \\ F_0 &= -\frac{32\sqrt{2}I\alpha^3}{9r^2} (SQ_0'' - CQ_0'); \end{aligned} \right\} \dots (9)$$

also

$$\therefore F_n' = -\frac{64\sqrt{2}I\alpha^3}{9r^2} S(Q_n''' - Q_n').$$

Substituting in  $R_n F_n' - R_n' F_n$ , and remembering that

$$SQ_n'' + CQ_n' - \left(n^2 - \frac{1}{4}\right) SQ_n = 0,$$

it will be found that

$$\begin{aligned} B_n &= -\frac{64\sqrt{2}I\alpha^3}{9\pi r^2} \left\{ C(P_n Q_n' - P_n' Q_n) + S(P_n' Q_n' - P_n Q_n'') \right. \\ &\quad \left. - \frac{2P_n'}{n^2 - \frac{1}{4}} \left( S - \frac{C^2}{S} \right) Q_n' \right\} \\ &= -\frac{64\sqrt{2}I\alpha^3}{9\pi r^2} \left\{ -\frac{\pi C}{S} + S(P_n' Q_n' - P_n Q_n'') + \frac{2P_n' Q_n'}{(n^2 - \frac{1}{4})S} \right\} \\ &= \frac{64\sqrt{2}I\alpha^3}{9r^2} \beta_n \text{ (say),} \end{aligned}$$

and

$$\beta_0 = \frac{1}{2} \left\{ \frac{C}{S} - \frac{S}{\pi} (P'_0 Q'_0 - P_0 Q''_0) + \frac{8P'_0 Q'_0}{\pi S} \right\}.$$

So also, in a similar manner,  $T_n F'_n - T'_n F_n$  gives

$$\begin{aligned} A_n &= \frac{64\sqrt{2}Ia^3}{9\pi r^2} \left\{ S(Q_n'^2 - Q_n Q_n'') + \frac{2Q_n'^2}{(n^2 - \frac{1}{4})S} \right\} \\ &= \frac{64\sqrt{2}Ia^3}{9r^2} \alpha_n \text{ (say),} \end{aligned}$$

with

$$\alpha_0 = \frac{1}{2\pi} \left\{ S(Q_0'^2 - Q_0 Q_0'') - \frac{8Q_0'^2}{S} \right\}.$$

The energy is

$$E = \frac{1}{2} \iint \psi \sigma \, dn \, dn' = \frac{Ia^2}{2\pi r^2} \int_{u_0}^{\infty} \int_0^{2\pi} \frac{\psi}{(C-c)^2} \, du \, dv.$$

The part of  $E$  depending on  $f$  is found by an easy integration to be

$$-\frac{4\pi R I^2}{3} \left( \frac{3}{4} + \operatorname{cosec}^2 \alpha \right).$$

The part depending on the infinite series is

$$\frac{Ia^2}{2\pi r^2} \sum B_n \int_{u_0}^{\infty} \int_0^{2\pi} \frac{T_n \cos nv}{(C-c)^{\frac{3}{2}}} \, du \, dv.$$

But from (9)

$$\begin{aligned} \int_0^{\pi} \frac{\cos nv}{(C-c)^{\frac{3}{2}}} &= \frac{4\sqrt{2}}{3S^3} (SQ_n'' - CQ_n') \\ &= \frac{4\sqrt{2}}{3} \frac{1}{S} \frac{d}{du} \left( \frac{Q_n'}{S} \right). \end{aligned}$$

Therefore the above

$$= -\frac{4\sqrt{2}Ia^2}{3\pi r^2} \sum B_n \int_{u_0}^{\infty} Q_n' \frac{d}{du} \left( \frac{Q_n'}{S} \right) du.$$

Now,

$$\int Q_n' \frac{d}{du} \left( \frac{Q_n'}{S} \right) = \frac{1}{2} \frac{Q_n'^2}{S} - \frac{1}{2} \int \frac{CQ_n'^2}{S^2} du;$$

also

$$\begin{aligned} \int \frac{CQ_n'^2}{S^2} du &= \int \frac{Q_n'}{S} \left( -Q_n'' + \left( n^2 - \frac{1}{4} \right) Q_n \right) du \\ &= -\frac{1}{2} \frac{Q_n'^2}{S} + \frac{1}{2} \left( n^2 - \frac{1}{4} \right) \frac{Q_n^2}{S} \\ &\quad - \frac{1}{2} \int \left\{ \frac{CQ_n'^2}{S^2} - \left( n^2 - \frac{1}{4} \right) \frac{CQ_n^2}{S^2} \right\} du; \end{aligned}$$

$$\therefore \int \frac{CQ_n^2}{S^2} du = -\frac{1}{3} \frac{Q_n^2}{S} + \frac{1}{3} \left( n^2 - \frac{1}{4} \right) \left\{ \frac{Q_n^2}{S} + \int \frac{C}{S^2} Q_n^2 du \right\};$$

$$\therefore \int_{u_0}^{\infty} Q_n \frac{d}{du} \left( \frac{Q_n}{S} \right) du = \left[ \frac{2}{3} \frac{Q_n^2}{S} - \frac{1}{6} \left( n^2 - \frac{1}{4} \right) \frac{Q_n^2}{S} \right]_{u_0}^{\infty} - \frac{1}{6} \left( n^2 - \frac{1}{4} \right) \int_{u_0}^{\infty} \frac{CQ_n^2}{S^2} du$$

$$= -\frac{2}{3} \frac{Q_n^2}{S} + \frac{1}{6} \left( n^2 - \frac{1}{4} \right) \left\{ \frac{Q_n^2}{S} - \int_{u_0}^{\infty} \frac{CQ_n^2}{S^2} du \right\}$$

where the functions outside the integral are functions of  $u_0$ .

It results that

$$E = -\frac{4\pi R I^2}{3} \left( \frac{3}{4} + \operatorname{cosec}^2 \alpha \right) - \frac{512R \cos^5 \alpha}{81\pi \sin^4 \alpha} \Sigma \beta_n \left\{ -2 \frac{Q_n^2}{S} + \frac{1}{2} \left( n^2 - \frac{1}{4} \right) \left( \frac{Q_n^2}{S} - \int \frac{CQ_n^2}{S^2} du \right) \right\},$$

and that the self-induction

$$= -\frac{8\pi R}{3} \left( \frac{3}{4} + \operatorname{cosec}^2 \alpha \right) + \frac{512R \cos^5 \alpha}{81\pi \sin^4 \alpha} \Sigma \beta_n \left\{ 4 \frac{Q_n^2}{S} - \left( n^2 - \frac{1}{4} \right) \left( \frac{Q_n^2}{S} - \int_{u_0}^{\infty} \frac{CQ_n^2}{S^2} du \right) \right\}.$$

It is seen that the question is not completely solved, as the integral  $\int_{u_0}^{\infty} \frac{CQ_n^2}{S^2} du$  has not been evaluated, as in the preceding case. Its value can, however, be approximated to when  $k$  is small.

If it be denoted by  $X_n$ , it can be shown that

$$(2n+1)^2 X_{n+1} - 16n X_n - (2n-1)^2 X_{n-1} = 8n \frac{C^2}{S} Q_n^2,$$

a difference equation, which if solved in a series ascending from  $Q_{n+1}$  would give  $X_n$ .

If we call the self-induction  $L$ , the energy is  $\frac{1}{2} L I^2$ .

If there are  $N$  turns of wire with a current  $i$ ,

$$I = Ni,$$

$$\text{and energy} = \frac{1}{2} N^2 L i^2,$$

whence the self-induction of such a coil is  $N^2 L$ .

8. For such a coil the values of the flux function are:—

Outside,

$$\psi' = \frac{64 \sqrt{2} R \cos^3 \alpha N i}{9 \sin^2 \alpha} \frac{1}{\sqrt{(C-c)}} \Sigma_0 \alpha_n R_n \cos n v;$$



Inside,

$$\psi = -\frac{8\pi R \cos^3 \alpha N i}{3 \sin^2 \alpha} \cdot \frac{S^3}{(C-c)^3} + \frac{64 \sqrt{2} R \cos^3 \alpha N i}{9 \sin^2 \alpha} \frac{1}{\sqrt{(C-c)}} \sum \beta_n T_n \cos n\nu,$$

where  $\alpha_n, \beta_n$  are the expressions given above.

When  $\alpha$  (or  $k$ ) is small, the values can be expressed in a few terms of a series of powers of  $k$  as in the former case. These values are as follows:—

$$\alpha_0 = -\frac{9\pi k^2}{4} \left(1 + \frac{13}{4} k^2 + \frac{221}{32} k^4\right),$$

$$\alpha_1 = \frac{45}{16} \pi k^4 \left(1 + \frac{17}{6} k^2\right),$$

$$\alpha_2 = \frac{105}{128} \pi k^6;$$

$$\beta_0 = \frac{3}{4} \left\{ 1 + (6L-9)k^2 + \frac{1}{2} \left(39L - \frac{255}{4}\right)k^4 + \left(\frac{663}{16}L - 66\frac{35}{64}\right)k^6 \right\},$$

$$\beta_1 = \frac{5}{2} \left\{ 1 + 3k^2 - \left(\frac{9}{4}L - \frac{57}{8}\right)k^4 \right\},$$

$$\beta_2 = \frac{7}{2} \left(1 + \frac{3}{2} k^2\right),$$

$$\beta_3 = \frac{9}{2}.$$

When  $k$  is not large, the integrals in the expression for the self-induction may be found approximately in a series of powers of  $k$ . If this be done, after some rather tedious calculations the value is found to be

$$4\pi R \left[ -\frac{7}{6} - \frac{2}{3} \frac{\cos^2 \alpha + 3 \cos^3 \alpha + 4 \cos^4 \alpha}{(1 + \cos \alpha)^3} + \frac{8 \cos^5 \alpha}{3(1 + \cos \alpha)^4} \left\{ 6L + \frac{1}{2} + (39L-5)k^2 \left( \frac{2115}{16}L - \frac{981}{64} \right) k^4 \right\} \right].$$

When  $k$  is very small this is  $\pi R(4L-7)$ .

The value of  $\psi'$  will give the coefficient of mutual induction between the circular coil and a thin circular wire with the same straight axis and with its plane parallel to the coil.

9. The same method of attack can be employed in dealing with gravitation potentials. Here

$$-\nabla^2\phi = -4\pi\sigma,$$

where  $\sigma$  is the density at the point  $(x, y, z)$ .

If  $f$  be a particular solution of this, and  $\phi$  denote the general solution of  $\nabla^2\phi=0$ , then at all points within the attracting body the potential  $= f + \phi_1$ , and at all points outside  $= \phi_2$ . Also  $\phi_1$  and  $\phi_2$  must be finite and continuous in their respective regions, and at the surface of the body the  $\phi_1$  and  $\phi_2$  and their first differential coefficients are continuous. These conditions suffice to determine  $\phi_1$  and  $\phi_2$ .

Take, for instance, the case of a uniform sphere. Inside  $\sigma$  is constant, and

$$\frac{d^2V}{dr^2} + \frac{2}{r} \frac{dV}{dr} = -4\pi\sigma.$$

A particular integral is

$$V = -\frac{2}{3} \pi \sigma r^2;$$

whilst the general solution is

$$V = A + \frac{B}{r}.$$

Hence:—

$$\text{Inside, } \phi = -\frac{2}{3} \pi \sigma r^2 + A + \frac{B}{r};$$

$$\text{Outside, } \phi' = A' + \frac{B'}{r}.$$

Inside,  $\phi$  is finite,  $\therefore B=0$ .

At the surface, when  $r=a$ ,

$$\phi = \phi', \quad \text{and} \quad \frac{d\phi}{dr} = \frac{d\phi'}{dr}.$$

Therefore

$$\left. \begin{aligned} A - \frac{2}{3} \pi \sigma a^2 &= A' + \frac{B'}{a} \\ -\frac{4}{3} \pi \sigma a &= -\frac{B'}{a^2} \end{aligned} \right\};$$

whence

$$A' = A - 2\pi\sigma a^2,$$

$$B' = \frac{4}{3} \pi \sigma a^3,$$

and

$$\phi = A - \frac{2}{3} \pi \sigma r^2,$$

$$\phi' = A - 2\pi\sigma a^2 + \frac{4}{3} \frac{\pi \sigma a^3}{r}.$$

If the density of the sphere is variable, the only difficulty is that of finding the particular integral  $f$ . As an example of variable density, take the case of a sphere in which the density varies as the square of the distance from a diametral plane. Here

$$-\nabla^2\phi = -4\pi cz^2,$$

$$f = -\frac{1}{3}\pi cz^4 = -\frac{1}{3}\pi cr^4 \cos^4 \theta,$$

and the general solution involves zonal harmonics ( $P_n$ ).

Hence, inside,

$$\phi' = -\frac{1}{3}\pi cr^4 \cos^4 \theta + \sum B_n r^n P_n,$$

and outside,

$$\phi = \sum \frac{A_n}{r^{n+1}} P_n.$$

Now,

$$\cos^4 \theta = \frac{8}{35} P_4 + \frac{4}{7} P_2 + \frac{1}{5}.$$

The surface conditions give at once

$$A_n = 0 = B_n \text{ for all } n > 4,$$

and

$$A_1 = A_3 = 0 = B_1 = B_3.$$

Also

$$\left. \begin{aligned} -\frac{1}{15}\pi ca^4 + B_0 &= \frac{A_0}{a} \\ -\frac{4}{21}\pi ca^4 + B_2 a^2 &= \frac{A_2}{a^3} \\ -\frac{8}{105}\pi ca^4 + B_4 a^4 &= \frac{A_4}{a^5} \end{aligned} \right\} \phi = \phi' \text{ when } r=a,$$

and

$$\left. \begin{aligned} -\frac{4}{15}\pi ca^3 &= -\frac{A_0}{a^2} \\ -\frac{16}{21}\pi ca^3 + 2B_2 a &= -3\frac{A_2}{a^4} \\ -\frac{32}{105}\pi ca^3 + 4B_4 a^3 &= -5\frac{A_4}{a^6} \end{aligned} \right\} \frac{d\phi}{dr} = \frac{d\phi'}{dr} \text{ when } r=a,$$

giving

$$\phi/\pi c = \frac{4}{15} \frac{a^5}{r} + \frac{8}{105} \frac{a^7}{r^3} P_2;$$

$$\phi'/\pi c = \frac{1}{15} (5a^4 - r^4) + \frac{4}{105} (7a^2 r^2 - 5r^4) P_2.$$

10. The gravitation potential of a tore has been recently

considered by Mr. Dyson \* by means of special functions and integration. It may be of use to indicate how the problem would be solved by toroidal functions and the differentiation method illustrated in this paper.

Inside the tore  $-\nabla^2 \phi = -4\pi\sigma$  with  $\sigma$  constant. A particular solution is

$$f = -\pi\sigma\rho^2 = -\pi\sigma a^2 S^2 (C-c)^{-2}.$$

Hence:—

$$\text{Outside, } \phi = \sqrt{(C-c)} \Sigma A_n P_n \cos nv,$$

$$\text{Inside, } \phi' = -\pi\sigma a^2 S^2 / (C-c)^2 + \sqrt{(C-c)} \Sigma B_n Q_n \cos nv.$$

$f$  must be expanded in a series of the form

$$f = \sqrt{(C-c)} \Sigma F_n \cos nv;$$

whence

$$\frac{\pi}{2} F_n = -\pi\sigma a^2 S^2 \int \frac{\cos nv}{(C-c)^{\frac{5}{2}}} dv.$$

This has been found above (9), viz.

$$F_n = -\frac{8\sqrt{2}}{3} \cdot \frac{\sigma a^2}{S} (S Q_n'' - C Q_n'),$$

$$F_0 = -\frac{4\sqrt{2}}{3} \cdot \frac{\sigma a^2}{S} (S Q_0'' - C Q_0').$$

Writing  $P_n$  for  $R_n$  and  $Q_n$  for  $T_n$  in § 3, we find

$$\left. \begin{aligned} A_n (P_n' Q_n - P_n Q_n') &= Q_n F_n' - Q_n' F_n \\ B_n (P_n' Q_n - P_n Q_n') &= P_n F_n' - P_n' F_n \end{aligned} \right\}.$$

But

$$P_n' Q_n - P_n Q_n' = \frac{\pi}{S}.$$

Hence

$$A_n = \frac{S}{\pi} (Q_n F_n' - Q_n' F_n),$$

$$B_n = \frac{S}{\pi} (P_n F_n' - P_n' F_n).$$

Inserting the values of  $F_n$  and  $F_n'$ , we get

$$A_n = \frac{16\sqrt{2}}{3} \sigma a^2 C \left\{ \left( n^2 - \frac{1}{4} \right) Q_n^2 - \frac{C^2 + 1}{CS} Q_n Q_n' - Q_n'^2 \right\}.$$

$$B_n = \frac{16\sqrt{2}}{3} \sigma a^2 C \left\{ \left( n^2 - \frac{1}{4} \right) \frac{\pi}{2C} + \left( n^2 - \frac{1}{4} \right) P_n Q_n - \frac{C^2 + 1}{CS} P_n Q_n' - P_n' Q_n' \right\}.$$

The external and internal potentials are thus completely found.

\* "The Potential of an Anchor Ring," Phil. Trans. 1893, pp. 43, 1041.

LVI. *On the Energy of the Amperian Molecule.* By A. P. CHATTOCK, *Professor of Physics, University College, Bristol,* and F. B. FAWCETT, *Associate of University College, Bristol*\*.

THE following experiments were undertaken for the purpose of determining, if possible, whether the molecular currents of Ampère are accompanied by motions of the molecules themselves. They were suggested during an attempt by one of us† to express certain physical properties of solids in terms of the ionic charges of their molecules.

The theory put forward by Weber, that Amperian molecules may be rotating charged carriers of electricity, lends itself at first sight to the view that the molecules of all matter, whether in the electrolytic form or not, carry upon them the charges they possess when in the condition of ions. It is only necessary to suppose that the molecules of a magnetic substance rotate with these charges in virtue of their heat motions, to account for the permanence of their magnetic moments at any given temperature.

Upon this supposition, if a bar of iron is saturated in a magnetic field, and this field is suddenly strengthened, the effect upon the iron will be two-fold. There will be a sudden decrease in the magnetic moments of the molecules corresponding to a decrease in their rates of rotation, and therefore to a cooling of the iron as a whole; and this will be followed by a slow return to their original condition as the iron receives heat from surrounding objects.

The result of Ewing's work on iron subjected to intense fields has been to show that no certain alteration in the value of  $I$  (the magnetic moment per cub. centim. of the iron) can be detected after saturation within the wide limits of field-strength which he employed. Upon the present hypothesis there should be no permanent alteration; and even the temporary fall of  $I$  on the first application of the field would be far too small to detect; its value being about  $5 \times 10^{-11}I$  when the magnetizing force is raised to 40,000 after saturation (see below).

But though the alteration of  $I$  is inappreciable, the accompanying fall of temperature is not; and we therefore decided to look for it. We were, moreover, encouraged to make the experiment by the publication of an interesting paper on the subject of ionic charges and their consequences by Dr. F.

\* Communicated by the Authors.

† *Phil. Mag.* Dec. 1892, p. 480.

Richarz\*, in which (p. 410) the author suggests rotating ions as the cause of molecular magnetism, and then gives quantitative support to his view by showing that the saturation values of  $I$  for magnetic metals are of the same order of magnitude as those calculated from reasonable assumptions as to the period of rotation of the molecules.

*Magnitude of the Effect sought.*

For simplicity of calculation, consider the molecules to have the form of thin rings of diameter  $\delta$  ( $=\frac{1}{2}10^{-8}$ ), rotating about their principal axes, carrying charges  $q$  ( $=3 \times 10^{-22}$  E.M.) and numbering  $n$  ( $=10^{25}$ ) to a cubic centimetre of iron.

Let the magnetic axes of these rings be parallel and similarly directed; *i.e.* let the iron be saturated and of magnetic moment  $I$  per cub. centim. It is easy to see that if  $V$  stands for the linear velocity of any point on a ring along its circumference,

$$V = \frac{I}{n} \cdot \frac{4}{\pi \delta^2} \cdot \frac{\pi \delta}{q} = \frac{4I}{n \delta q} \quad \dots \dots \dots (i.)$$

Suppose now that the field by which the molecules are held in position is suddenly increased by an amount  $H$ . The number of lines of force which will enter each ring per centim. of its circumference is  $\frac{H}{\pi \delta} \cdot \frac{\pi \delta^2}{4} = \frac{H \delta}{4}$ , and the momentum imparted thereby to the matter of the ring is consequently  $\frac{H \delta}{4} q$ . From this it follows that if  $v$  is the change produced by this process in the original velocity ( $V$ ) of a ring of mass  $m$ ,

$$v = \frac{H \delta q}{4m} \quad \dots \dots \dots (ii.)$$

Now the ratio  $\frac{v}{V}$  is the fraction by which the magnetism in the iron decreases when  $H$  is increased. If we put  $H=40,000$  (Ewing's maximum value about) and  $I=1500$ ,  $\frac{v}{V}$  comes out to be  $5 \times 10^{-11}$ , as stated above.

From (i.) and (ii.) it is also easy to calculate the loss of heat in the iron due to any increase of  $H$ .

$$\text{Loss of kinetic energy of the } \left. \begin{array}{l} \text{rings in ergs per cub. centim.} \end{array} \right\} = \frac{1}{2} nm V^2 - \frac{1}{2} nm (V-v)^2, \\ = nm V v - \frac{1}{2} nm v^2;$$

and since  $v$  is negligible compared with  $V$ , the second term

\* Wied. Ann. lii. p. 385 (1894).

vanishes. Hence, as  $nmVv = IH$  from (i.) and (ii.), it follows that

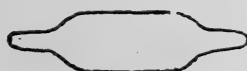
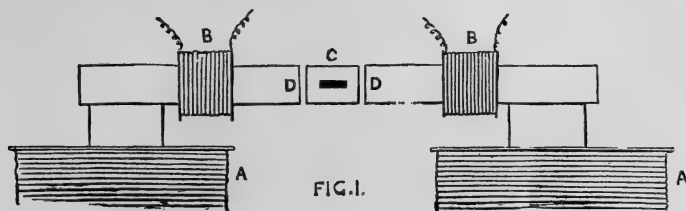
$$\left. \begin{array}{l} \text{Loss of heat in calories} \\ \text{per cub. centim.} \end{array} \right\} = \frac{IH}{J}, \quad \dots \dots \dots \text{(iii.)}$$

where  $J$  is Joule's equivalent. For an increase of  $H$  of 250 at saturation this would mean a fall of temperature of about one hundredth of a degree C.

This is a well-known expression for magnetic-field energy; and though obtained in this somewhat roundabout manner, it is of course quite independent of any hypothesis as to the source of the energy being in the motion of the molecules or elsewhere. The above equations simply suggest a mechanical explanation, in the case of magnetic molecules, for the fact that, when energy is put into surrounding space by starting any current  $A$  (say the source of  $H$  in the above), it is less when  $A$  is alone than it is if a second current  $B$  (the molecular current) is already flowing in its neighbourhood; the difference being wholly derived from the source of  $B$  (which, according to the present hypothesis, is the kinetic energy of the molecule) *provided B does not change in strength during the process*. If it does—in other words, if the second term in the above expression does not vanish—part of the extra field-energy is derived from the source of  $A$ , and calculation becomes practically impossible.

### Description of Apparatus.

After several unsuccessful attempts to obtain reliable values, the arrangement shown in fig. 1 was adopted.  $AA$  are the



upper portions of the coils of a large electromagnet.  $BB$  are small auxiliary coils for the purpose of producing an alteration

in the magnetizing force experienced by the iron under test; the latter being contained in a zinc box C, which was filled and surrounded with cotton-wool and placed between the poles DD.

The test-piece consisted of a bundle of fine iron wires lying parallel to the lines of force, into the centre of which was introduced one end of a "line" thermopile. The other end of the pile was surrounded by a coil of silk-covered copper wire all in one length, which was similar in size and shape to the iron test-piece.

The actual size and shape of the mould in which the separate plates of the alloys forming the pile were cast is shown in fig. 2. The plates were about  $\frac{1}{2}$  millim. thick, and were composed alternately of the alloys\* 32 parts bismuth + 1 part antimony, and 12 parts bismuth + 1 part tin. They were placed side by side with mica to separate them, and were soldered at their pointed extremities, which were then covered with goldbeater's-skin. Fourteen pairs were used to form the pile.

By this means the junctions formed a blunt knife-edge and were brought well into the centre of the iron wire; the mass of the pile being at the same time kept small at that point, while it was large enough outside to prevent undue resistance to the thermal current.

The galvanometer, connected through a mercury commutator with the pile, was at a distance of nearly 20 yards from the electromagnet, and its circuit was provided with a small variable E.M.F. to counterbalance accidental thermal currents. The scale was read by a telescope, and a motion of a tenth of a division could be easily detected.

#### *Results of the Experiments.*

The constant saturating field between DD (fig. 1), produced by exciting the main coils A, was first measured by the earth-inductor method and found to be about 2800 C.G.S.; and a separate current was then sent through the coils B of such a strength that on reversing it the main field was altered by 166 C.G.S. units (H in equation iii.). The currents required to produce these fields were also measured, so that they might be reproduced for the experiment.

After passing current through the exciting coils for a couple of hours to obtain a steady temperature, the method of experiment was as follows:—

Galvanometer-readings were taken every 20 seconds, the current in B being at the same time reversed every 5 minutes,

\* Boys, 'Cantor Lectures,' 1889, p. 18.



so as to alternately heat and cool the iron if the effect looked for existed. In this way fifteen readings were obtained between every pair of reversals. It was found, however, that a small inductive effect on the galvanometer-circuit occurred at each reversal, and could not be quite got rid of. The needle always kicked from 0.5 to 1 and oscillated. On the other hand, it so happened that the period of oscillation of the needle was almost exactly 60 seconds. We therefore divided the fifteen readings into five groups of three; and taking the mean of each three we assumed it to represent the average position of the needle during one minute. Five reliable readings were thus obtained at intervals of 0.5, 1.5, 2.5, 3.5, 4.5 minutes after each reversal of the B current. Nine such reversals formed a "set." At the end of a set the connexions of the galvanometer were reversed, to eliminate a possible direct magnetic effect on the needle of the galvanometer, and the set was repeated. Two such sets thus constituted a complete experiment.

In the following table the mean values of the differences between the readings in the strong and in the weak field, taken at 0.5, 1.5, 2.5, &c. minutes after alteration of the field, are given for the four sets of two complete experiments. The final mean values of these differences are thus each dependent on 108 separate readings of the galvanometer.

TABLE I.

Time in minutes after alteration of field between the values 2717 and 2883. }	0.5	1.5	2.5	3.5	4.5
Expt. I. { Set 1 .....	-0.64	-0.47	-0.42	-0.38	-0.33
{ Set 2 .....	-0.43	-0.24	-0.30	-0.16	-0.31
Expt. II. { Set 1 .....	-0.30	-0.33	-0.36	-0.11	-0.10
{ Set 2 .....	-0.38	-0.18	-0.28	+0.07	-0.08
Final mean differences .....	-0.44	-0.31	-0.34	-0.15	-0.21

The effect of commutating the galvanometer upon the sign of the differences has been allowed for in the table by reversing the signs of Set 2 in each experiment. The - sign to every difference except one means that, except in that case, the cross-wires stood more to the left of zero when the pile was in the strong field than when it was in the weak one.

To determine the thermal meaning of this fact, we next sent a small momentary current through the copper-wire coil mentioned above as being upon the other end of the pile. The galvanometer was connected as for Set 1. A motion of the

cross-wires to the right resulted. Hence, if the differences observed were due to the iron, an increase of the magnetic field must have warmed it—*just the reverse of what theory required.*

The volume and resistance of the copper in the coil upon the pile were known. By sending the proper current through the coil for one second, it was possible to produce in the copper the number (0.006) of calories per cub. centim. which ought to have been produced in the iron by weakening the field, viz.  $\frac{IH}{J}$ . The result was a deflexion which reached a maxi-

mum value of 3.8 at the end of about 75 seconds after the copper had been warmed, and died away in less than 6 minutes. As the two ends of the pole were as nearly alike as possible, this value gave a rough idea of the deflexion to be expected. The observed effect of 0.44 was thus about nine times too small and in the wrong direction.

These results were obtained at the end of the Christmas vacation, and at this point we were obliged to remove our apparatus for the term's work.

Two possible causes for the effect we had observed occurred to us. One, that the alteration in field-strength had altered the resistance of the pile, and therefore of the current passing through it. The other, that the iron had not been quite saturated throughout its length, and that hysteresis effects had been superposed upon the one we were looking for. We therefore undertook a fresh series of measurements this summer with better appliances. The galvanometer was rendered absolutely dead-beat with a large mica vane, so that each reading was complete in itself. The distance between the pole-pieces was decreased from 3.0 to 2.65 centim., by which means the strength of the main field was increased to 3200 C.G.S., and the length of the iron test-piece was increased until there was only 0.5 millim. clearance between its ends and the pole-faces, instead of 7 millim. as before.

Direct measurement now showed that the iron was thoroughly saturated, and that the value of  $I$  for it was 1640.

A further improvement consisted in the fact that the iron wire was itself silk-covered and all in one length, so that the artificial heating for calibration could be performed upon the specimen itself, and a far more accurate indication obtained of what to expect from the variations of the magnetic field.

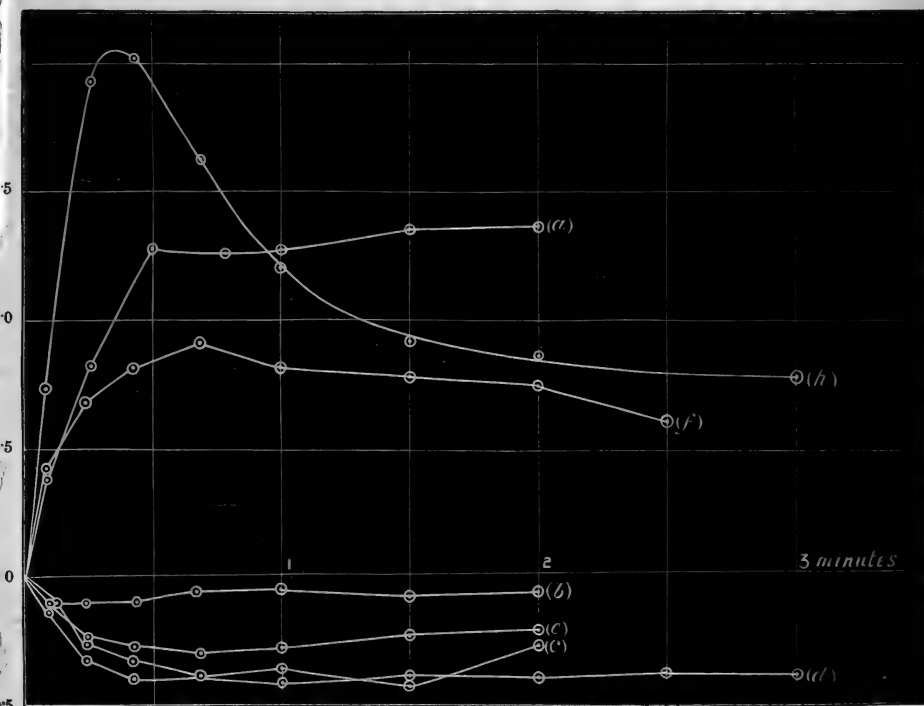
Slight movements of the test-piece on altering the field were now found to give rise to small thermal effects, due doubtless to an alteration in the flow of heat from the exciting coils through the pole-pieces into the pile brought about

thereby. The pile and test-piece were therefore together embedded in a slab of paraffin wax, 2.55 centim. thick, through which passed two brass pins 2.65 centim. long and 0.3 centim. in diameter, which were melted into the wax on either side of the test-piece, and served to prevent any relative motion between it and the pole-pieces.

On trying this soon after the paraffin had set, the following readings were obtained in the right\* direction; that is to say, they pointed to a cooling of the iron when the field was strengthened.

$t=$	0	5	15	30	45	60	30	60	secs
	0.0	+0.31	+0.83	+1.29	+1.26	+1.26	+1.35	+1.37	

Here  $t$  stands for the time in seconds after altering the field between the values 3310 and 3090 either way ( $H=220$ ).



The readings (which correspond to the 'final mean differences' of Table I.) are plotted in curve (a). Curve (h) in

\* The + sign is used in what follows to indicate that the readings are in accordance with theory, and *vice versa*.

the same diagram represents the effect of heating the iron wire by means of a current flowing through it for one second, and of the proper strength to produce  $\frac{1640 \times 220}{J}$  calories per cub. centim. of the iron. The points which determine this curve are the mean values of several consistent observations.

The following day the readings were in the wrong direction (curves *b* and *c*), nothing having been altered in the mean time. Thinking that the alterations in the field-strength might still be capable of producing some relative movement of the pile and the strands of the test-piece, the effect of which had been altered by the hardening of the paraffin during the night, we caused the paraffin to penetrate the interstices of the iron wire by means of the air-pump, and the apparatus was then placed in position and subjected to a field of about 3000 units for 5 hours while it cooled. Readings taken next day were still negative, and to about the same extent as before (curves *d* and *e*). The substitution of a solid cylinder of iron for the iron wire did not affect matters. Relative motion of test-piece and pile seemed therefore to be excluded.

The clearance between pole-faces and test-piece was next increased from 0.5 to 3.5 millim. without altering the result; from which we inferred that the values obtained could not be due to a slight yielding of the paraffin slab when the field was altered, the distance from slab to poles being too great to be affected thereby in this case. Neither could they be due to a direct effect of the field upon the resistance or E.M.F. of the pile, for we found that they were independent of the direction of any permanent current which might be flowing through the pile during the observations.

It only remained therefore to suppose that our results were attributable to a change in the conductivity for heat of the system pile-test-piece; the flow of heat through it from the exciting current being alternately checked and accelerated as the field was altered. That a flow was actually occurring from the iron into the pile and on through it to its other end, was shown by the direction of the E.M.F. required in the galvanometer circuit to balance the permanent effect of the pile. It was due to the fact that the pile was too long to allow of its being wholly between the poles at the same time that the test-piece was in a uniform part of the field.

The correctness of this view was proved by showing that the sign of the effect changed with the direction in which the

heat flowed through the pile. By passing hot or cold water through holes in the pole-pieces we were able to alter the flow at will. The following are the results obtained:—

TABLE II.

Seconds after altering field .....	Effect observed.			
	0	5	15	30
Warm water passed for about 20 minutes and then stopped.	0·0	-0·33	-0·73	-0·87
After 5 minutes .....	0·0	-0·12	-0·42	-0·50
After 25 minutes .....	0·0	-0·14	-0·25	-0·26
After 45 minutes .....	0·0	-0·13	-0·16	-0·13
Ice-cold water passed through next day and kept flowing ...	0·0	+0·01	+0·15	+0·15
20 minutes later .....	0·0	+0·04	+0·11	+0·22
Water stopped.				
20 minutes later .....	0·0	-0·11	-0·20	-0·15

These numbers are each the mean of ten determinations, and show clearly the alteration of sign from - to + as the flow of heat changed from the iron-pile to the pile-iron direction. They accord with the sign of a set of readings we took, in which the end of the pile remote from the iron was warmed by a tube carrying a stream of tepid water (curve *f*); and they also explain the change of sign which occurred while the paraffin slab was cooling (p. 479).

Having thus traced our first results to the unsymmetrical arrangement of the pile, the obvious course was to put it in such a position that the flow of heat through it was avoided altogether, and to repeat our original readings. This we tried to do, but without success. It was easy to reduce the flow to a very small amount, but quite impossible to keep it so for more than a few minutes at a time. We venture to think, however, that the curves obtained are sufficient to prove the absence of the molecular effect sought for. A comparison of the curve for artificial heating with the others shows that the peak, which is so marked a feature in the former, is not found in the latter. It is true that if only the normal curves *b*, *c*, *d*, *e* are considered, it might be urged that the peak is perhaps absent because it is neutralized by an equal and opposite peak in the effect which gives the readings their negative sign. But if this were so, it should be doubly present in the curves

$a$  and  $f$ , where the two peaks would be in the same direction. That this is not the case seems to us to render it practically certain that it does not exist at all\*. In other words, that *if the molecular currents are due to a spinning motion of ionic charges, this motion is not inseparably connected with a spinning of the molecules themselves.*

LVII. *A New Method of Magnetizing and Astaticizing Galvanometer-Needles.* By F. L. O. WADSWORTH†.

[Plate XIII.]

A GREAT deal of attention has been devoted by many eminent physicists to the improvement of the galvanometer, and it has in consequence been brought to perhaps as high a degree of delicacy and excellence as any of our standard physical instruments. It is vain to hope for any great advance in sensitiveness in existing types, but there will always be a steady improvement in details and methods of construction.

One of the first essentials in securing a maximum degree of sensitiveness in a galvanometer of the Thomson type is to secure the maximum intensity of magnetization in the magnetic system. The maximum attainable will depend on three factors:—first, on the form of the individual magnets and their arrangement with reference to each other; second, on the quality of the steel used in making the magnets, and the method of hardening and tempering the same; and third, on the method of magnetization. I have found that the intensity of magnetization, and hence the sensitiveness of the galvanometer, depends on this last factor to a greater degree than has usually been supposed, and that by using the method which will presently be described the sensitiveness of a given galvanometer may be doubled and in some cases more than quadrupled. This results not so much from an improvement in the magnetizing process *per se* as from the method of application.

The usual method of making the astatic system of the Thomson galvanometer is to build up each member of the system from a number of individual bar-magnets, each of which is hardened and magnetized as strongly as possible between the poles of a powerful electromagnet, either during

\* The only way out of this conclusion is to suppose that the peak has been neutralized by some effect which we have overlooked, and which does not change its sign with the direction of the heat-flow. But this is unlikely.

† Communicated by the Author.

the process of hardening and tempering or subsequently\*. During the process of building up, the individual magnets are subjected to various demagnetizing influences, the most serious of which are the jars and blows received in the process of mounting, and the proximity of other magnets during the process of astaticizing. The resultant strength of each member of the finished system is therefore considerably less than it would be if the individual magnets were magnetized to their saturation-point. Prof. Threlfall† avoided this difficulty by magnetizing each member of the system *in situ*, using for this purpose two separate electromagnets, one for each member.

It was this which first suggested to me the present method, which differs from the preceding in that but one electromagnet is used for simultaneously magnetizing both members of the system. The advantage of this is that both members, when being magnetized, form part of one and the same magnetic circuit, and hence, barring magnetic leakage (which may be reduced to a minimum by proper design of circuit), are necessarily in fields of precisely the same strength for all magnetizing forces—one essential condition for securing astaticism, or in preserving it when once established and remagnetization is desirable. When separate electromagnets are used for each member, it is necessary in order to secure this condition that the field of each be of exactly the same strength, an end which requires for its accomplishment the taking of unusual precautions (described in the paper referred to) in the selection of material, the winding of the coils, &c. The single electromagnet device is therefore considerably simpler to construct and more convenient to use.

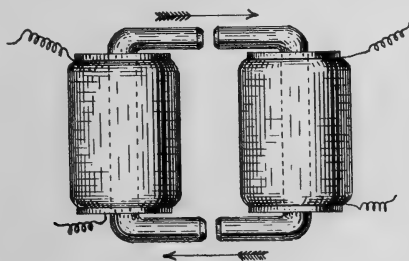


Fig 1

Fig. 1 is an elevation of the electromagnet in the form in

\* Simultaneous magnetization and hardening does not seem to possess any advantages over the ordinary method. See Holz, Wied. Ann. vii. (1879).

† "Measurement of High Resistance," Phil. Mag. vol. xxviii. p. 452 (1889).

which it was first used. It consists simply of two pieces of round iron  $\frac{3}{8}$  inch diameter, each bent into the shape of a very shallow U, with legs about 1 inch long and back or yoke  $2\frac{3}{4}$  inches long (this being the distance between the centres of the two members of the astatic system), wound with about 350 turns of No. 18 magnet-wire. With a current of 5 amperes in the magnetizing coils, and a separation between the poles of the two halves of 3 millim., the density in the iron cores amounts to about 5000 C.G.S.

The system to be magnetized is laid on its back on the edge of a narrow strip of wood *b* mounted on a board B (figs. 1 & 2, Plate XIII.). This strip is a very little wider than the length of the needles of the system, and of such a height that the top edge is just below the centre of the poles of the electromagnet, the two yokes of which rest on the supporting base. Thin strips of glass or mica are cemented on each side of the central strip opposite the poles of the magnet, to prevent the latter from touching the needles. The coils of the two yokes are so connected that the whole forms a single magnetic circuit with the two air-gaps *m, n*, in each of which lies one of the members of the magnetic system, so that when the current is turned on by means of a key, K, they are strongly and equally magnetized in opposite directions, as required. In order to secure the maximum permanent magnetization, the strength of the field should be suddenly increased to a maximum and then gradually decreased, several times in succession, either by varying the strength of the current in the coils by means of a rheostat, or, better, by varying the distance between the two poles\*, tapping the support with a light hammer or block of wood when the magnetic induction is at a maximum, in order to assist in "setting" the molecular structure. The magnetization being finished, the system is lifted carefully from its support, hung by means of its attached fibre in a glass tube large enough to allow it to swing freely, and tested for astaticism.

\* In no case should the magnetizing current be broken suddenly when the poles are close to the needles, or the strength of the latter may be very considerably weakened, if not destroyed, by the sudden recoil of the field. See Auerbach, *Wied. Ann.* xiv. (1881), and Fromme, *Wied. Ann.* v. (1878):—"Auerbach lays down as a general principle that when the variation of the magnetizing force is slow and continuous the velocity of the transition does not influence the final magnetization; but sudden transition causes the final magnetization to be less or greater than that obtained by gradual transition, according as the passage is from a greater to a less or from a less to a greater force." (*Encyc. Brit.* art. "Magnetism," p. 260.)

In this connexion see also paper by Lord Rayleigh, *Phil. Mag.* [4] vols. xxxviii. & xxxix. (1869, 1870).



Usually, owing to difficulties of construction, one member will be slightly heavier and hence magnetically stronger, and the magnetic planes will be slightly inclined to each other; the amount and direction of which inclination can be ascertained by noting the setting of the system with reference to the magnetic meridian.

The planes of the members should first be brought to parallelism by a slight twisting of one of them on its support. A good way to do this is to take two bar-magnets, N, S (fig. 2), and bring first one and then the other up against the side of the glass tube, as in fig. 2, opposite the magnetically stronger of the two members, which will be drawn against the wall of the glass tube toward the magnet first brought up, say N. If a right-handed twist is needed to bring the two planes to parallelism, the two magnets are held as shown, in front of the axis of the tube; if a left-handed one, behind the axis, as indicated by the dotted lines. Then the magnet N is quickly removed and the member is drawn toward S against the inclined wall of the tube, giving it a blow which tends to twist it clockwise on the axis of suspension and at the same time to slightly weaken it. Repeating this operation a few times will soon suffice to bring about the required degree of parallelism unless the cement which attaches the member to the staff be too hard and dry, in which case a slight heating of the surrounding tube with a hot block of copper or a Bunsen-flame will be necessary to render the cement slightly plastic.

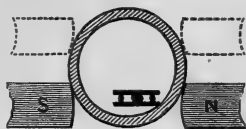


Fig. 2.

Parallelism having been secured (which is determined by the plane of the system lying in the magnetic meridian), the relative magnetic strengths of the two members are tested by determining the time of vibration. Generally, if the system has been made up with a proper degree of care, the strengths of the two members will be so nearly equal that it will only require a very weak directing magnet placed some distance above or below the system to secure almost perfect astaticism.

But if it is desirable to secure this without the use of such a magnet, it will be necessary to add to the weaker of the two systems a minute fragment of steel (a very short piece broken off from one of the finest watch hair-springs answers well), and then to remagnetize the whole as before, taking care of course to magnetize in the same direction. The whole operation requires at the most but a few hours' work by an experienced manipulator, and the success of this method may be judged by the results which have been obtained by its use.

The first galvanometer experimented upon was a fine Thomson instrument, whose coils were wound by While, and whose needle system was made by Very\*. The magnetic system was built up of hollow cylindrical magnets, rolled up out of the thinnest sheet-steel, heated red-hot in fused ferrocyanide of potassium, and hardened in mercury in a powerful magnetic field. The system was then astaticized by the usual method of stroking with a weak bar-magnet. Every care was taken to secure the maximum intensity of magnetization. The constant of the galvanometer in its most sensitive state was  $C = 1.5 \times 10^{-9} \dagger$ .

The best value of the constant of the Allegheny galvanometer already referred to was  $C = 1.3 \times 10^{-9}$ . On October 23 the magnetic system was removed and remagnetized, and reastaticized by the method described above. No other change was made. The new constant after magnetization was  $C = 8 \times 10^{-10}$ , an increase in delicacy of nearly 100 per cent.

The second galvanometer to whose magnetic system this method of treatment was applied was one constructed by Queen and Co. especially for the Observatory. The magnetic system had very nearly the same dimensions as the one already described, but the individual magnets were solid. The method of hardening and magnetizing was not described by the makers. The constant for this galvanometer as received from them was:—

$C = 1.6 \times 10^{-9}$  for coils in series,  $R = 309$  ohms,

$C = 5.5 \times 10^{-9}$  for coils in parallel,  $R = 19.2$  ohms.

The needle was removed and remagnetized by the new method and the constant redetermined. The new constant was:—

$C = 1 \times 10^{-10}$  for coils in series,

$C = 3.4 \times 10^{-11}$  for coils in parallel.

Part of the immense improvement here is due to a more accurate centering of the coils, to the magnetic system, and to a reduction of the excessive damping; yet with a most

\* This instrument was a duplicate of the celebrated Thomson galvanometer, with Very hollow magnets, used by Langley at Allegheny in his bolometric work; and which was considered at that time to be the most sensitive (for its resistance) in existence. See paper by S. P. Langley, "On hitherto unrecognized Wave-lengths," *Phil. Mag.* [5] xxii. p. 149 (1886).

†  $C$  = current in amperes which produces a deflexion of 1 millim. on a scale at the distance of 1 metre, when the time of a single swing is ten seconds.

liberal allowance for the influence of these changes, the sensitiveness was increased fully ten times by the remagnetization.

This would seem to indicate either that the first magnetization had been very inefficient, or that the needle in transit from Philadelphia to Washington had been accidentally subjected to some very strong demagnetizing influence. It serves to show, however, the importance and necessity of some such ready and efficient means of remagnetizing the systems of galvanometers in which a high degree of sensitiveness and not absolute constancy is required. Steel magnetized to the degree of intensity here attained will of course gradually lose a part of its magnetism, but not more (in my experience) than 10 or 20 per cent. in many months, if carefully handled. This small loss is not of importance compared with the gain in sensitiveness secured, as the original strength may at any time be quickly and easily restored or even slightly increased\* by remagnetization.

The advantage of the method which specially commends it to general laboratory use is the simplicity of the apparatus required. The whole arrangement may be made in any laboratory in a single afternoon. The same electromagnets may be used for systems of varying dimensions by adding adjustable pole-pieces. But if many systems are to be treated, a more convenient although more elaborate arrangement, like that shown in Plate XIII. figs. 3 & 4, will be desirable. In this the magnetic system is held lightly between two long jaws of copper *a, a*, adjustable in width by means of the screw *b*. An adjustable fork or table *c*, which may be replaced by a clamp if desired, serves to carry the fibre support.

The two halves of the electromagnet, which may be wound as before, or with four coils as here shown, are carried on arms *d, e*, pivoted at *f*, so that they may be easily swung apart or brought together, the motion being made symmetrical with respect to the jaws *a, a* by means of the links and sliding block. The lower set of poles are adjustable on the yokes for systems of different lengths, and the whole is mounted on an L-shaped base, which may be placed so that the needle is either vertical as shown in the figure, or horizontal.

This method has also been applied with much success to the initial magnetization of some new systems for the same galvanometer already described, and for the new very sensitive one which is described in a subsequent paper. A further

\* Up to a certain point repeated magnetization increases the permanent magnetism. See experiments of Frankenheim, *Pogg. Ann.* cxxiii. (1864); and Fromme, *Pogg. Ann.* vii. (1875), Wied. *Ann.* iv. (1878).

advantage which this method possesses over the usual one in the case of a new system is that, in making it up, we have only *unmagnetized* needles to handle ; an advantage which those who have had much to do with this kind of work can readily appreciate.

Astro-Physical Observatory,  
Washington, D.C., February 1893.

LVIII. *On the Effects of Magnetic Fields on the Electric Conductivity of Bismuth.* By JAMES B. HENDERSON, B.Sc.\*

[Plates XV. & XVI.]

THAT magnetic fields have an effect on the electric conductivity of metals was noticed first in the year 1856 by William Thomson† (Lord Kelvin), who was led to suspect it from the effects which he had discovered magnetization to have on the thermoelectric properties of metals. He experimented on iron and nickel, and found in both an increase of resistance along the lines of force, and a diminution perpendicular to them.

Bismuth was first experimented on by Tomlinson‡, who found an increase of resistance due to longitudinal magnetization of Bi wire, and he found a similar increase in Fe, Ni, Co, and steel wires. Later investigations in this subject have been made by Righi§, Hurion||, Leduc¶, Ettingshausen and Nernst\*\*, Ettingshausen††, Goldhammer‡‡, Lennard and Howard§§, and Lennard|||; but the last of these is the one which has the most important bearing on the present investigation.

In this Lennard used spirals of Bi wire, in all fifteen spirals being tested, whose wires varied from 0.2 to 0.4 millim. in diameter, and from 50 to 150 centim. in length, the respective resistances varying from 6 to 25 Siemens units. The resistance was determined by the Wheatstone-bridge direct-current method, and also by the method using

\* Communicated by the Author.

† Math. and Phys. Papers, ii. p. 307.

‡ Phil. Trans. 1883.

§ *Journ. de Physik.* iii. p. 355 (1884).

|| *Compt. Rend.* xcvi. p. 1257 (1884).

¶ *Compt. Rend.* xcvi. p. 673 (1884).

\*\* *Wien. Ber.* xciv. part ii. p. 560 (1886).

†† *Wien. Ber.* xcv. p. 714 (1887).

‡‡ *Wied. Ann.* xxxi. p. 360 (1887); xxxvi. p. 804.

§§ *Electro-technische Zeitschrift*, ix. p. 341.

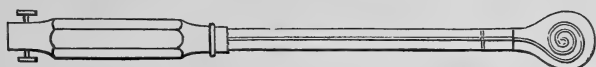
||| *Wied. Ann.* xxxix. p. 619 (1890).

alternating current and telephone, and a remarkable difference was found in the resistances obtained by the different methods. Two kinds of Bi were used, one chemically pure and the other containing traces of Fe and Zn, but differences were not more than those due to observational errors. Deviations from the mean values amounted to 1 per cent. The temperature varied from  $10^{\circ}$  to  $25^{\circ}$  C., and once was  $0^{\circ}$  C.

The present investigation was instituted to determine definitely the relation between the magnetic field and the resistance of Bi wire going to much higher field-intensities than had ever been experimented with, and also to determine the influence of temperature on that relation if any was found. The investigation was started purely from the scientific standpoint, but the importance of it to the practical application of Bi wire as a field-tester was not lost sight of.

Owing to the purity with which Bi wire is now prepared for instruments for magnetic-field testing, and the convenient form for experimenting which these field-testers offer, it was determined to use them in this investigation. Two such were employed, the spiral of one having a diameter of about 18 millim. and a resistance of 24 ohms, and that of the other a diameter of 6 millim. and a resistance of about 9 ohms. The form of the instrument is shown in fig. 1.

Fig. 1.

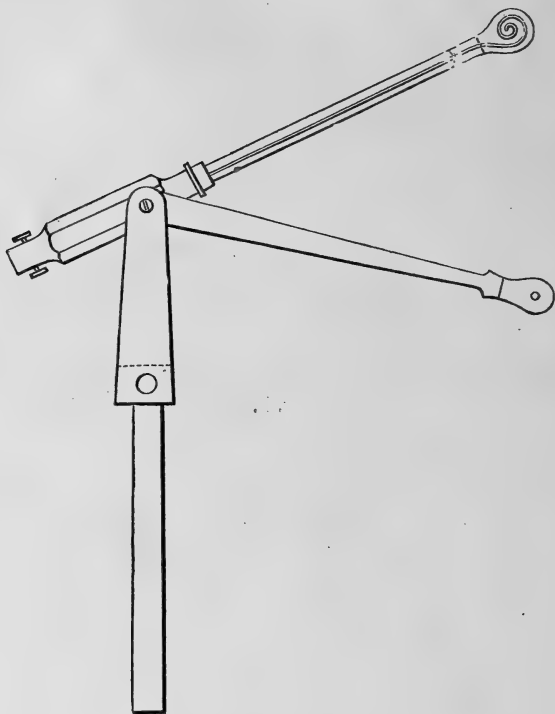


The magnetic fields were obtained by means of a Ruhmkorff electromagnet, and the very highest field-intensities from the large ring-electromagnet lately designed by H. du Bois\* for the production of very strong fields for experimental purposes. With the large spiral the ordinary dome-shaped pole-pieces belonging to the Ruhmkorff magnet were used, the holes in them being first blocked up with pieces of soft iron to render the field as uniform as possible. For the small spiral special pole-pieces were prepared, which were designed to fit the ring-electromagnet, but by using a pair of flat poles with them they also fitted the Ruhmkorff magnet. They had an angle of  $60^{\circ}$ , and their faces, which were 7 millim. in diameter, were held at a distance of 1.5 millim. apart by means of a brass casting to which both pole-pieces were rigidly attached. This casting consisted of two thick rings held rigidly parallel and coaxial by means of two stout

\* *Magnetische Kreise*, p. 277; *Wied. Ann.* li. (1894); *Phil. Mag.* May 1894.

distance-pieces, and to each ring one of the pole-pieces was soldered, the inner surfaces of the rings being conical to receive them (see fig. 4). The distance-pieces were not at opposite ends of a diameter of the rings, but one was displaced a few degrees round the circumference of the ring to allow of the introduction of the spiral and the ballistic coil, which turned about the same horizontal axis and in the same vertical plane (see fig. 2).

Fig. 2.



The ballistic method was used to measure the field, the galvanometer being of the form designed by du Bois and Rubens\*, used with the four 20-ohm coils in parallel. It was standardized by means of the induced current produced in a fine coil placed at the centre of a long straight solenoid of thick wire, when a current through the latter was made or broken†. The constants of both coils being known and the current in the solenoid measured, the induced current

\* Wied. *Ann.* xlviii. p. 234 (1893).

† For particulars of apparatus see Lehmann, Wied. *Ann.* xlviii. (1893).

was easily calculated and the constant of the galvanometer obtained from it.

The ballistic coil for the large spiral consisted of one turn of wire mounted on one of the mica plates between which the Bi spiral was cemented, and embraced the whole area of the spiral, which area was determined by accurate measurement. The ballistic coil for the small spiral consisted of four turns of very fine copper wire wound side by side on a small wooden cylinder about 6 millim. in diameter and rather less than 1.5 millim. long, so that with the thin ends to keep the wire in position the whole coil could pass between the poles. From the exact dimensions of the wooden cylinder and of the wire the constant of the coil was calculated.

These two ballistic coils were compared in a uniform field between large flat pole-pieces, and the ratio of their constants, experimentally determined, agreed within one half per cent. with the calculated value.

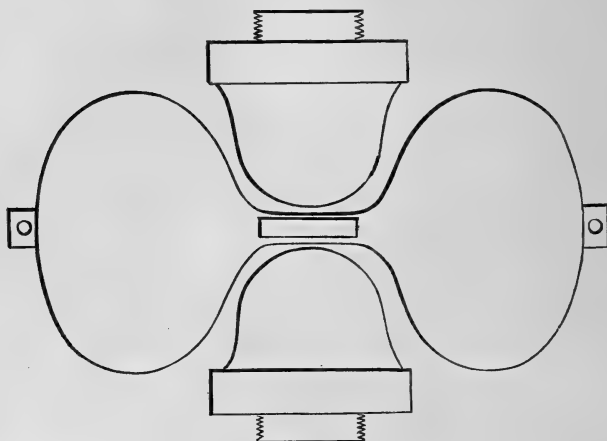
The resistance of the spirals was measured always by the Wheatstone-bridge with direct currents and galvanometer.

At first no arrangement was made and no precautions taken to keep the temperature constant, as other experimenters had found no influence due to it; but after some results had been obtained, it was seen that these varied among themselves beyond the limits of observational error wherever the temperature had varied, and so a method of keeping it constant became necessary.

For each spiral a watertight copper case was made, that for the large spiral having the dimensions  $95 \times 26 \times 5$  millim. and for the small one  $95 \times 9 \times 1$  millim., and these were fitted over their respective spirals but so as not to touch the copper rods which served as terminals to them. For each spiral a water-bath was made, that for the large one consisting of a cylindrical copper box with a horizontal section resembling a lemniscate in form, the thin part in the centre going between the poles. Fig. 3 shows a plan of the box between the poles. Since it was necessary to remove the spiral quickly from between the poles to measure the field, the ballistic coil being fastened to it, and still to keep the temperature constant, the spiral was fixed in the narrow part of the box and the box mounted on vertical guides, so that by means of a cord passing over a pulley the whole bath with the contained spiral and ballistic coil could be suddenly raised clear of the magnet. In each side of the bath a stirrer was placed. With this apparatus experiments were made with ice, and with water the temperature of the room in the bath, but none could be made with hot water, as the spiral could not be heated above  $30^{\circ}\text{C}.$

about which temperature the cement between the mica plates melted ; but in the small spiral this cement was changed for

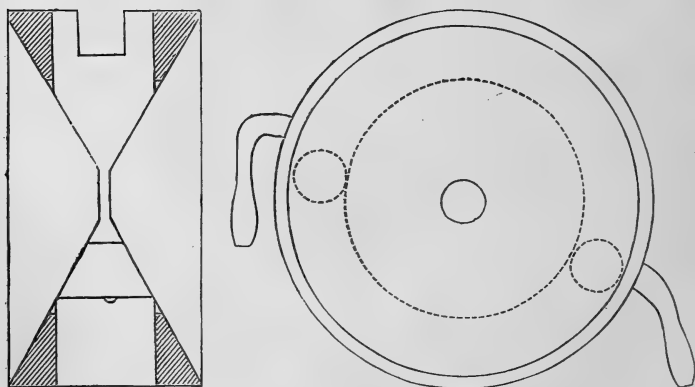
Fig. 3.



shellac, and it could therefore be heated to  $80^{\circ}$  C. On this account, therefore, as also on account of the higher fields in which it could be placed, the results obtained from the small spiral are more interesting and important.

In the case of the water-bath for the small spiral (see fig. 4)

Fig. 4.



the pole-pieces themselves were made to form part of the vessel. The two brass rings to which the poles were soldered were connected outside by a cylindrical brass tube of large



diameter, which was pushed over them and soldered to both, thus forming a closed cylindrical vessel with the pole-pieces as ends. A slit made at the top for about one quarter of the circumference served to admit the small spiral or the ballistic coil, and two extra holes in it with brass tubes fitted in them served as inlet and outlet for a flow of water. In this way it was possible to have a constant flow of water over the poles and spiral.

The temperature of the spiral was measured by means of a thermoelectric junction placed beside it inside the copper case; and the same galvanometer was used to measure the temperature and field, it being never required for both purposes simultaneously.

Experiments were first of all made with the large spiral, using either ice or water of the temperature of the air in the bath, and the two series given below in Table I. for 0° and 18° C. are chosen from a number done in this way.

TABLE I.

0° C.			18° C.		
Magnetic Field. C.G.S.	Resistance. Ohms.	Percentage-Increase of Resistance.	Magnetic Field. C.G.S.	Resistance. Ohms.	Percentage-Increase of Resistance.
0	22.43	0.0	0	24.0	0
970	22.8	1.7	770	24.23	0.8
1220	23.02	2.7	960	24.38	1.5
1700	23.49	4.7	1740	24.85	3.4
2800	24.85	10.8	2860	25.96	8.2
4120	26.74	19.2	4160	27.55	14.8
7110	31.41	40.0	7190	31.36	30.7
6340	30.13	34.4	6260	30.22	25.9
6830	30.81	37.4	6880	30.95	29.0
7350	31.67	41.3	7270	31.56	31.5
7970	32.55	45.1	7930	32.40	35.0
8700	33.79	50.7	8740	33.53	39.7
9690	35.33	57.5	9650	34.85	45.2
10910	37.37	66.7	10950	36.72	53.0
13070	40.43	80.3	12750	38.95	62.3
Series at 0° and 18° C. with large spiral.					

In all the experiments with this spiral the constancy of the temperature was tested by taking the resistance of the spiral when raised clear of the poles each time the field was measured; and the temperature could be got very exactly from the temperature-coefficient curve. Throughout a series the temperature never varied more than one degree, and for the greater part of the series it was constant. Pl. XV. fig. 5

represents the above series in graphic form, where the ordinates represent resistances and the abscissæ field-intensity.

It will be seen that the curves take a form somewhat resembling an hyperbola with its axis parallel to the resistance coordinate ; and that the rate of increase of the resistance, or the inclination of the curve to the horizontal, diminishes as the temperature increases, so that each curve cuts all the others but not in the same point, as will be made clearer in considering the results from the small spiral. The third columns in the foregoing table give the percentage increase of resistance, and these are shown in graphic form in Pl. XV. fig. 6. Here the curves all pass through the origin and have a similar form to those described above, the inclination to the horizontal being less as the temperature increases.

With the large spiral, tests were made for hysteresis of resistance by taking two series at the same temperature, one with ascending values of the field-intensity and the other with descending ; but the results obtained agreed within the limits of observational error, and so, if hysteresis does exist, it must be of a small order of magnitude.

Tests were also made for time-lag of resistance by finding the resistance in zero-field, then, after being placed in a magnetic field, again in zero ; but no difference could be noticed after times comparable with several seconds. That there is such time-lag after very short intervals of time appears in Lennard's results with the alternating current and telephone, which show that the resistance found in this way is a function of the period of alternation ; and it is also shown by some experiments lately made by Rubens in Berlin to determine if vibrating spirals of Bi wire in magnetic fields could be used for microphonic purposes ; but his results proved the negative.

In the foregoing results the highest field obtained with the large spiral has been 13,000 C.G.S., that is, over an area of about 268 square millim., and was obtained with the pole-pieces 9 millim. apart, with a current of 30 amperes. In the investigation the current was obtained either from six accumulators, or from the Berlin supply-mains at a potential of 108 volts. With the fine pole-pieces fields of 28,000 were obtained with about 10 amperes from the accumulators, and 33,000 with about 30 amperes from the mains ; and with the same pole-pieces in H. du Bois's ring-magnet and a current of 45 amperes, a field of 39,000 was obtained.

Thus there was a full range up to 39,000 C.G.S. available, and the following table gives the resistance of the small spiral at 18° C. in the full range of field-intensities.

TABLE II.

Magnetic Field. C.G.S.	Resistance. Ohms.	Resistance with that in zero-field as unity.	Percentage-Increase of Resistance for comparison with Table I.
0	8.57	1.0	0
5830	10.54	1.227	22.7
6310	10.74	1.253	25.3
6830	11.04	1.290	29.0
7790	11.47	1.341	34.1
8880	12.06	1.407	40.7
10410	12.83	1.496	49.6
12500	13.97	1.630	63.0
15710	15.60	1.830	
20450	18.57	2.160	
23480	20.02	2.333	
26820	21.50	2.508	
27450	21.76	2.540	
27820	22.07	2.568	
28370	22.37	2.609	
29270	22.65	2.643	
30090	23.20	2.704	
31270	23.77	2.772	
32730	24.40	2.846	
32820	24.32	2.837	
33300	24.78	2.893	
35800	26.29	3.070	
36600	27.03	3.160	
38900	28.56	3.334	
Series at 18° C. with small spiral.			

To enable a comparison to be made with the series for the large spiral at 18° C. the percentage increase in fields up to 13,000 is also given, and these values are plotted along with those for the large one in fig. 6, the crosses denoting the points got from the small spiral. The diagram shows that the two spirals agree at this temperature.

Pl. XV. fig. 7 represents the series given in Table II. in graphic form. It will be seen that the resistance is more than tripled in the highest field at 18°; and for a lower temperature it would have a still higher value, and, *vice versa*, for a higher temperature, a lower.

The four highest fields in the above series were obtained by means of the ring-magnet, and as the apparatus was arranged specially to suit the Ruhmkorff, the same exactitude does not apply to these readings as to the others. The magnet had a very large influence on the galvanometer, which was eliminated by repeating each experiment with the current reversed

in the magnet and taking the mean ; and on the whole these four points can have a possible error of about 2 per cent.

To determine the influence of temperature on the resistance in the magnetic field two methods were made use of. First, the temperature was kept constant, or as constant as possible, and the resistance taken in different fields ; and second, the field was kept constant and the temperature varied, or the temperature-resistance curves in different fields determined. The latter method proved much more successful than the former, as it was much easier to keep the field constant than the temperature, and the particulars and results of the latter method only will be given.

For the fields the current from the accumulators alone was used, and by taking currents up to about 7 amperes constant fields up to 23,000 C.G.S. were obtained.

In the experiments a flow of water at  $0^{\circ}$  C. was sent over the poles and spiral, and the resistance taken at the lowest temperature reached, which was when the galvanometer became steady, and usually represented about  $9^{\circ}$  C. The flow of water was then stopped and the temperature of the bath slowly raised by a small flame to  $80^{\circ}$  C., the temperature and resistance of the spiral being read off at intervals. The constancy of the field throughout the experiment was noticed by observing no change of current through the magnet, as shown by an ampere-meter.

In this way temperature-resistance series were obtained for the fields as given in Table III., varying from zero to 23,000, in all nine different series, which are represented graphically in Pl. XVI. fig. 8.

From the diagram it will be seen that the inclination of these curves to the horizontal diminishes as the field increases, being positive at first, then zero, and then negative ; but at the same time it is also evident that with increasing field the curves deviate more and more from the straight line form, to which the curve in zero-field or the ordinary temperature-coefficient curve approximates ; so that those curves which have a horizontal part within the temperature limits of these experiments are only horizontal for a small distance, which represents a minimum value of the resistance. Such minimum values occur at higher and higher temperatures as the field increases. Thus, for example, the curve for a field of 9600 has its minimum value about  $35^{\circ}$ , that for 11,500 about  $50^{\circ}$ , and the one for 14,300 is horizontal at  $85^{\circ}$ . Thus, reasoning from analogy, it would seem that all the curves have a minimum value, the higher the field the higher being the temperature at which the minimum occurs, and *vice versa*.

Pl. XVI. fig. 9 represents five curves for the temperatures

TABLE III.

Zero Field.		4900 C.G.S.		5800 C.G.S.	
Temperature C.	Resistance. Ohms.	Temperature C.	Resistance. Ohms.	Temperature C.	Resistance. Ohms.
0	8.02	5.7	9.91	8.2	10.45
6.6	8.22	8.3	9.94	32.2	10.70
7.0	8.23	16.1	10.03	42.6	10.89
12.3	8.40	27.1	10.22	57.8	11.17
16.0	8.51	37.1	10.40	67.8	11.36
21.7	8.69	41.3	10.49	74.0	11.54
28.8	8.91	45.7	10.58	80.0	11.64
36.2	9.16	50.5	10.68		
44.3	9.43	54.1	10.77		
54.0	9.76	58.1	10.86		
61.9	10.04	62.1	10.96		
92.0	11.09	66.7	11.05		
		70.7	11.14		
		74.7	11.26		

7200 C.G.S.		9600 C.G.S.		11,500 C.G.S.	
Temperature C.	Resistance. Ohms.	Temperature C.	Resistance. Ohms.	Temperature C.	Resistance. Ohms.
7.6	11.22	10	12.53	9.2	13.63
28.2	11.27	23.4	12.4	23.8	13.34
36.2	11.36	—	12.35	33.4	13.25
44.2	11.45	59	12.49	—	13.15
51.8	11.55	69	12.59	73.6	13.25
58.2	11.64	77.2	12.68	82.6	13.34
64.0	11.74				
69.2	11.83				
74.8	11.92				
79.8	12.02				

14,300 C.G.S.		18,500 C.G.S.		22,700 C.G.S.	
Temperature C.	Resistance. Ohms.	Temperature C.	Resistance. Ohms.	Temperature C.	Resistance. Ohms.
9.4	15.22	9.6	17.58	10.8	19.93
12.4	15.13	16.2	17.21	22.6	19.00
17.2	14.94	21.0	16.92	26.4	18.72
20.2	14.85	25.0	16.73	29.4	18.53
23.2	14.75	29.0	16.55	34.6	18.27
27.2	14.66	34.4	16.37	43.4	17.80
36.4	14.47	39.2	16.18	52.6	17.40
48.4	14.28	45.8	15.98	61.6	17.12
60.4	14.2	49.6	15.88	68.0	16.93
75-84	14.16	53.6	15.79	77.0	16.74
		58.2	15.70	81.4	16.64
		63.6	15.61		
		70.8	15.51		
		80.0	15.42		

$10^{\circ}$ ,  $30^{\circ}$ ,  $50^{\circ}$ ,  $65^{\circ}$ , and  $80^{\circ}$ , deduced from the above temperature-resistance curves represented in fig. 8, and forming cross curves to them.

The three variables—resistance, field-intensity, and temperature—could thus be made the three coordinates, and a smooth regular surface obtained giving the value of any one of the variables if the other two are known. Pl. XVI. fig. 8 represents sections of this surface perpendicular to the field coordinate, fig. 9, sections perpendicular to that of temperature; and in fig. 10 are represented sections perpendicular to the resistance-coordinate, or equi-resistance lines of the surface. It is evident that fig. 9 represents a family of curves with a variable parameter, namely the temperature, and the envelope of this family is interesting. It represents the projection on the field-resistance plane of the locus of the minimum points considered in fig. 8, or gives the connexion between the field and resistance for which a minimum value of the latter takes place; or, to put it still another way, at these values of the resistance and field the former is independent of small increases or decreases of temperature. Thus for each field there is a certain temperature at which increases or decreases of temperature of one or two degrees have no effect on the resistance. The projection of this locus on the field-temperature plane would be represented in fig. 10 by a curve through all the points where the tangents are parallel to the temperature coordinate—that is, the points where the field is a maximum.

A few words have still to be added on the practical application of Bi wire to the measurement of magnetic fields.

We have seen that the phenomenon of alteration of resistance of Bi wire in magnetic fields is greatly influenced by temperature, and therefore for anything like exact determinations the temperature must be known. A suitable combination of thermometer with the spiral would therefore remove difficulties, and this can be most conveniently arranged by winding a spiral of copper or platinum side by side with the Bi spiral, and from its resistance determining the temperature.

In closing, I desire to express my great indebtedness to the late Prof. Kundt and Drs. du Bois and Rubens for the help which they have given me by putting private apparatus at my disposal, and for the advice which I have received from them from time to time.

Physical Institute, Berlin University,  
July 20, 1894.

LIX. *Notices respecting New Books.*

*The Outlines of Quaternions.* By Lieut.-Colonel H. W. L. HIME.  
(Longmans, Green, and Co. 1894.)

IT is becoming more and more clearly recognized that a vector algebra is the proper mathematical method for treating physical problems; and it may confidently be said that in Hamilton's Quaternions we find such a vector analysis of a most powerful and flexible character. O'Brien, a contemporary of Hamilton, constructed a vector analysis similar in many respects to Hamilton's, but lacking the solidarity and flexibility which apparently the quaternion alone can give. Recent attempts to follow where O'Brien led have served but to bring out in stronger light the transcendent superiority of the Hamiltonian system. This is said advisedly; for the recent vector analyses which have been presented to the world are all unconscious plagiarisms of O'Brien's.

But there is another class of mathematicians who object to the quaternion because it does not seem to fit in with the general drift of modern analysis. It is undeniable that, on the purely mathematical side, there has been little systematic advance in quaternions since Hamilton's own time. But is not this due rather to the timidity of man than to any inherent weakness in the system? In the later chapters of Tait's treatise, which abound in original and striking applications, there are hints and suggestions that might easily be developed into memoirs and even treatises by the purely analytical mind. The truth is that many a seemingly simple quaternion expression or equation, when translated into ordinary analytical symbols, assumes a form that mocks at the bravest analyst; and certain quaternion equations, sufficiently interpretable, have never yet been expressed in Cartesian coordinates.

If we except Hamilton's, Tait's, and McAulay's papers and treatises, most of the literature of the subject has been a restatement of known results. Lieut.-Colonel Hime's book confessedly belongs to this class. It is intended for the student. A knowledge of geometry and algebra such as may easily be obtained in a secondary school is sufficient to enable the learner to read intelligently nearly the whole of the book. The processes of differentiation are discussed in a short chapter; but they are not used to any marked extent in the geometrical illustrations given further on. Within the limits assigned, Colonel Hime has given us a book which cannot fail to be of service in popularising the study of quaternions. Its value would have been enhanced had it contained at the end of every chapter a selection of exercises for the student's private work. As the author himself points out in the closing paragraph, it is not in simple geometrical applications that the peculiar power of quaternions is displayed. It is certain, however, that no candid mind can read the sections devoted to spherical geometry and trigonometry without being

struck with the extraordinary simplicity of the quaternion mode of attack. Once the quaternion in its true geometrical significance is understood, we need never refer—except in wondering awe—to a treatise on spherical trigonometry.

With so much that is worthy of praise in Colonel Hime's book, we gladly refrain from criticism of minor details, which are often a mere question of taste. But it is otherwise with a few really serious faults, which seem eminently fitted to perplex the student. Such a fault is the whole of paragraph 11. Whatever it is, it is not quaternions; indeed it is inconsistent with nearly all the other paragraphs of the book. As a quaternion equation, equation (8)

$$i=j=k=\sqrt{-1}=-i=-j=-k$$

is simply nonsense. Having already taught us that  $i, j, k$  are coperppendicular unit vectors or right versors (the identification of which is one of the bursts of genius in Hamilton's calculus), what reason has the author for declaring that  $i=j=\&c.$ ? "Equation (8)," we are told, "asserts that all unit-vectors in the first power are equal, as *versors*, in respect to angle." In short, versors are to be equated when their angles are equal. For consistency's sake, Colonel Hime should use the equation  $Uq = Ur$  as meaning *only*  $\angle q = \angle r$ . Further on we are told that "the symbol  $\sqrt{-1}$  represents them  $[i, j, k]$  *only* in their character of indeterminate right versors." But  $i, j, k$  have already been *defined* in anything but an indeterminate manner. This arbitrary robbing a symbol of its most characteristic feature, so that it no longer is what it was defined to be, is contrary to the whole genius of—Common Sense. What would the Cartesian analyst say to the equation

$$x=y=z=\sqrt{+1}=-x=-y=-z,$$

which is certainly less irrational than equation (8).

Again, at the foot of page 76 we meet with the equation

$$\frac{\delta}{\beta} = \sqrt{\frac{\gamma}{\beta}},$$

which is asserted to mean that  $\delta$  bisects the angle between  $\beta$  and  $\gamma$ . Then we read:—"This equation may be written  $\delta^2 = \gamma\beta$ , where  $\delta$  is called the Mean Proportional between  $\beta$  and  $\gamma$ ." Now we are told in previous sections that  $\delta^2$ , the square of a vector, is a scalar; and that  $\gamma\beta$ , the product of two different vectors, is a quaternion. The legitimate conclusion is that a scalar is equal to a quaternion! The equation  $\delta^2 = \gamma\beta$  really means that  $\beta$  and  $\gamma$  are *parallel* vectors, to whose tensors the tensor of  $\delta$  is the geometric mean. If it mean ought else it cannot be a quaternion equation. But, anyhow, it has no business here. The true transformation of the equation first given is  $\delta\beta^{-1} = \gamma\delta^{-1}$ , a totally different thing.

We hope that the author will in future editions delete the second form of this equation entirely, recast the whole of paragraph 11, and root out the altogether obnoxious equation (8).



The book will then be a very serviceable introduction to quaternions, although we should like to see a more logical and thorough laying down of the foundations of the calculus. Especially does the whole question of vector and versor require careful presentation, else will the triple dynasty of antiquaternionic vector analysis let loose their invective, their scorn, and their specious pleadings.

## LX. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 423.]

May 9th, 1894.—Dr. Henry Woodward, F.R.S., President,  
in the Chair.

The following communications were read:—

**T**HE following communications were read:—

1. 'Carrock Fell: a Study in the Variation of Igneous Rock masses.—Part I. The Gabbro.' By Alfred Harker, Esq., M.A., F.C.S.

The paper opens with an account of the general relations of the intrusive rock-masses of the district, and proceeds to deal more particularly with the gabbro, which forms the earliest intrusion.

A petrological description of the Carrock Fell gabbro is followed by a study of the variations observed in different parts of the mass. The rock becomes progressively more basic from the centre to the margin, passing from a quartz-gabbro with as much as  $59\frac{1}{2}$  per cent. of silica to an ultrabasic type with as little as  $32\frac{1}{2}$ . The latter in extreme cases contains nearly 25 per cent. of iron-ores, partly titaniferous. This is compared with the igneous iron-ores described by Vogt in Scandinavia, &c., and the probable physical cause of the remarkable variation in the gabbro is discussed.

Other modifications of the gabbro are briefly noticed, due on the one hand to metamorphism of the rock by a somewhat later intrusion of granophyre, on the other hand to the gabbro-magma having enclosed considerable masses of the basic lavas of the district, which are themselves highly metamorphosed.

2. 'The Geology of Monte Chaberton.' By A. M. Davies, Esq., B.Sc., F.G.S., and J. W. Gregory, D.Sc., F.G.S.

The importance of the Chaberton district, as affording a key to the general geology of the Cottians, is explained, and the opinions of previous observers referred to. The mountain was examined from three sides—that of the Grand Vallon; the approach from Mont Genève by the Col de Chaberton; and that of the Clos des Morts Valley. The following are the conclusions arrived at:—

(1) The well-known Chaberton serpentine is intrusive into the calc-schists, and yields fragments to the *cargneules* of the Trias: it is therefore a *pre-Triassic* intrusion.

(2) There are on the mountain other fairly basic schistose rock

(quartz-chlorite-schists) which cut the Trias, and are therefore *post-Triassic*.

(3) The contorted beds in the Clos des Morts Valley are fossiliferous limestones, and it is from them that the fallen blocks previously recorded were derived. The only recognizable fossil is *Calamophyllia fenestrata*, Reuss, a characteristic coral of the Gosau Beds. In spite, therefore, of the doubts of Kilian and Diener, the opinion expressed by Neumayr as to the existence of Cretaceous rocks in this part of the Alps is confirmed.

(4) The earth-movements of the mountain are described: they include ordinary folds, inversions, faults, and an important thrust-plane.

(5) It is suggested that in addition to the two series of intrusive rocks above-mentioned as pre- and post-Triassic, a third series of late Cretaceous or Tertiary date may be represented in the Mont Genève and Rocciavré masses.

3. 'Cone in Cone; its Structure, Varieties, &c.' By W. S. Gresley, Esq., F.G.S.

The author describes cone-in-cone structure occurring in the Portage Shales of Pennsylvania, and gives details concerning the nature of the structure as seen in these shales. He criticises the explanation of Mr. J. Young as to the origin of the structure, and concurs in a great measure with the views of those who have suggested that the formation was due to pressure acting on concretions.

May 23rd.—Dr. Henry Woodward, F.R.S., President,  
in the Chair.

The following communications were read:—

1. 'On the Stratigraphy and Physiography of the Libyan Desert of Egypt.' By Captain H. G. Lyons, R.E., F.G.S.

The Nubian Sandstone, wherever seen, rests unconformably on the old rocks called by Sir J. W. Dawson Archæan, and the author finds no case of alteration of sandstone by these rocks, though in one case it is altered by an intrusive dolerite.

The author considers the Nubian Sandstone to be an estuarine deposit which was formed on an area afterwards gradually invaded by the Cretaceous sea. He considers the whole of the sandstone in the region which he has examined to be of Cretaceous age.

He describes a series of anticlinals, one set running W.N.W.—E.S.E., and the other N. by E. and S. by W. Many springs of the oases seem to occur along these anticlinals, owing to the beds which contain the water being brought nearer to the surface. Historical evidence is discussed which points to the Nile having reached a higher level in Nubia than it does at present, and it is suggested that variations in the level of the river were caused by earth-movement opposing obstructions to the river's flow.

The sandstone of Jebel Ahmar near Cairo is described, and its occurrence over a wide area west of Cairo is recorded. The author considers its age to be later Miocene. He believes that, with the

exception of some erosion after the deposition of the Eocene beds, the greatest erosion, including the cutting-out of the Nile Valley, took place in Miocene times, while a certain amount, bringing the area to its present condition, was done in Quaternary times. This agrees with the observations of the French geologists in Algeria. The origin of the silicification of the fossil trees of the sandstone-deposits is discussed, and the action of water containing sodium carbonate suggested as a cause.

2. 'Notes on the Geology of South Africa.' By D. Draper, Esq., F.G.S.

The district here considered includes Natal, Zululand, Swaziland, the S.E. part of the Transvaal, and the Eastern part of the Orange Free State and of Basutoland. Physically it comprehends:—1. The Drakensberg Range; divided into—*a*, Mountain portion; *b*, Hill-covered plateau; *c*, Highveld plateau: 2. The terrace along its foot: 3. The coast-belt. Their main features and characteristics are described. The geological formations are:—

Karoo Beds.	Upper.	1. Volcanic Beds.
		2. Cave Sandstone.
		3. Red Beds.
		4. Molteno Beds.
		5. Beaufort Beds.
	Lower.	6. Ecce Beds.
Palæozoic.	{	7. Dwyka (Ecce) Conglomerate. [Bokkeveld Beds, wanting.]
		8. Gats Rand (Zuurberg) Quartzite.
		9. Dolomitic Limestone.
		10. Table-mountain Sandstone.
		11. Malmesbury Schists.
		12. Gneiss and Granite.

No. 1. Briefly noticed. 2. This caps the hills of the plateau (1, *b*); and has yielded fossil fishes (described by Mr. A. S. Woodward, F.G.S.) in the Orange Free State. 3. These are exposed in the O. F. S., at Harrismith, about 100 feet thick, and containing a bone-breccia from which reptilian remains were described by Prof. Owen in 1854. Northwards the Red-beds change to a dark grit; and siliceous tree-stumps occur in the upper part. 4. These are the well-known coal-bearing beds of the Highveld plateau (1, *c*) and Natal, including the terrace (2) north of the Tugela River, and Zululand. The lower 500 feet of these beds in Natal carry coal better than that of the Highveld, but have been let down to a lower level (about 2000 feet). In Natal they thicken northwards. On the coast-line in Natal and Zululand portions are at a still lower level and dip seaward at 20°. Anthracite occurs at St. Lucia Bay. 5. These form hill-side crags along the edge of the terrace (2); and die away northwards near the Pongolo River. 6. The 'Pietermaritzburg Shales' of Dr. Sutherland also die out northwards near that river. 7. The 'Glacial Conglomerate' of Dr. Sutherland; exposed in high crags in the deeper gorges of the terrace (2); stratified and

ripple-marked; horizontal inland, but near the coast dipping seaward with the overlying beds. A patch, much ripplea and containing few pebbles or boulders, lies horizontal in the coast-belt (3) of Zululand and Swaziland at least 1000 feet lower than the main body seen along the terrace (2). No. 7 stretches from St. Johns River, through Pondoland and Natal to Zululand, thins out and disappears near the Pongolo. Intrusive and flat diorites were noticed in it. A definite list of the strata of this conglomerate, where it is 138 feet thick in Zululand, is given; and the author does not regard it as of glacial origin. No. 9 is treated of in the next paper.

3. 'On the Occurrence of Dolomite in South Africa.' By D. Draper, Esq., F.G.S.

A peculiar calcareo-siliceous rock, near Lydenburg, described by Messrs. Penning and Crutwell as 'Chalcedolite,' and a similar rock mentioned by Mr. Penning, F.G.S., as overlying the 'Black-reef Series' of the Megaliesberg formation, are recognized as a dolomite. Mr. C. Alford, F.G.S., has described a 'calcareous quartzite,' as passing into dolomite and ultimately into chert, and known as the 'Elephant-rock' in Transvaal, sometimes cavernous with underground waters. From his own experience Mr. Draper has recognized the 'Elephant-rock' in the Potschefstroom, Lichtenburg, Malmani, and Lydenburg districts as a real dolomite, with interstratified siliceous bands, weathering into a brown earth like mangarese oxide, and superficial siliceous débris. It has its place between the Table-mountain Sandstone and the quartzite of the Gats Rand (=Zuurberg Quartzite of the Cape). It has auriferous veins in Malmani and Lydenburg. Dr. Schrenck has noticed a similar dark-blue dolomitic limestone in Great Namaqualand. The deep water-holes in it in Malmani are comparable with those found by F. Galton in West Central Africa. The great caves in Mashonaland may belong to it. The extensive tufaceous deposits in Griqualand-West, the Transvaal, and Orange Free State were probably derived from this extensive dolomite.

4. 'Contributions to the Geology of British East Africa.' By J. W. Gregory, D.Sc., F.G.S.

The author describes moraines, striae, glacial lake-basins, perched blocks, and *roches moutonnées* below the present limits of the glaciers of Mount Kenya, which he maintains indicate the existence of a 'calotte' or ice-cap extending at least 5400 feet farther down the mountain than the termination of the present glaciers, and possibly farther, for in the belt of forest detailed observations could not be made.

He agrees that this more extensive glaciation was produced by a greater elevation of Mount Kenya, and that any theory of universal glaciation is unnecessary, and indeed opposed by many facts in African geology.

He discusses the probable influence of this former glaciation on the meteorological conditions of the surrounding area and the distribution of its flora and fauna.

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AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

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DECEMBER 1894.

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LXI. *On the Rate of Oxidation of Phosphorus, Sulphur, and Aldehyde.* By THOMAS EWAN, B.Sc., Ph.D., late 1851 Exhibition Scholar in Chemistry at the Owens College\*.

INTRODUCTION.

ACCORDING to our present knowledge the velocity with which a chemical change takes place is dependent on the concentrations of the substances taking part in the change, and the connexion between the two is of such a nature that a greater concentration corresponds to a greater velocity.

Under these circumstances it is of great interest that in a number of instances oxygen gas appears to act chemically more vigorously, that is with greater velocity, when it is dilute than when it is more concentrated.

The first mention of this behaviour, so far as I know, was made by Fourcroy†. He says that at the ordinary temperature and pressure pure oxygen is without action on phosphorus, although ordinary air acts vigorously. In 1798 van Marum‡ found that a piece of phosphorus glowed much more brightly in rarefied than in ordinary air, and that it even took fire at very low pressures if surrounded by a little cotton-wool. These observations were confirmed and extended by subsequent observers.

\* Communicated by the Author.

† *Mémoires de l'Académie des Sciences*, 1788.

‡ *Verhandelingen uitgegeven door Teyler's Tweede Genootschap*, 10 (1798).

According to Thorpe and Tutton\* phosphorous oxide,  $P_4O_6$ , shows phenomena in presence of oxygen gas which possess the strongest resemblance to those exhibited by phosphorus itself. They suggest that the more rapid reaction at lower pressures is due to the increased volatility of the phosphorous oxide.

Joubert† noticed similar behaviour with sulphur and arsenic.

Friedel and Ladenburg‡ found that a mixture of silicon hydride,  $SiH_4$ , and oxygen inflames spontaneously on decreasing its pressure, and Houton de Labillardière§ had previously made a similar observation with phosphine ( $PH_3$ ).

Van de Stadt|| mentions that nickel carbonyl,  $Ni(CO)_4$ , appears also to behave similarly. Reicher and Jorissen¶ found, however, that it is still spontaneously inflammable in oxygen under a pressure of 13 atmospheres.

Engelmann\*\* found that certain Bacteria show a preference for a certain definite concentration of dissolved oxygen. Greater or smaller concentrations seem to be less favourable to their existence.

Labillardière's observation with phosphine was repeated by van't Hoff††, who found that at ordinary temperatures the spontaneous inflammation of the mixture took place when the partial pressure of the oxygen was about  $\frac{1}{10}$  atmosphere. The gases were preserved over a saturated solution of calcium chloride. When the partial pressure of the oxygen was higher or lower than  $\frac{1}{10}$  atmosphere, only a slow combination took place.

H. J. van de Stadt‡‡ in 1893 investigated the subject more fully in order to find how the velocity of the slow combustion which precedes the explosion changes with the concentration. He found that the reaction proceeded slowly and with a nearly constant velocity, which showed no noticeable acceleration until the explosion-pressure was reached, when the explosion took place, sometimes at once, sometimes on standing.

This reaction was therefore not a very suitable one for the

\* Journ. Chem. Soc. 1890, p. 569.

† Thèses présentées à la Faculté des Sciences de Paris, 1874.

‡ Ann. Ch. Phys. [4] xxiii. p. 430 (1871).

§ Ann. Ch. Phys. vi. p. 304 (1817).

|| Zeit. Phys. Chem. 1893, xii. p. 322.

¶ Maandblad voor Natuurwetenschappen, No. 1 (1894).

\*\* Botanische Zeitung, 1882, p. 320.

†† Etudes de Dynamique Chimique, p. 60 (1884).

‡‡ Zeit. Phys. Chem. 1893, xii. p. 322.

study of the connexion between the velocity of the change and the concentration of the oxygen. For this reason, and at the suggestion of Professor van't Hoff, I took up the study of the velocity of the reaction between phosphorus and oxygen.

#### RATE OF OXIDATION OF PHOSPHORUS IN MOIST OXYGEN.

##### (a) *Behaviour in Air.*

Some measurements have already been recorded by Ikeda\*. He found that at  $19^{\circ}$  the oxidation of phosphorus in moist air takes place with a velocity which is nearly proportional to the concentration of the oxygen. At the lower pressures the reaction went a little faster than is required by exact proportionality.

My first experiments were made in the same way as those of Ikeda. The apparatus consisted of a bottle of  $1\frac{1}{2}$  to 2 litres capacity with two necks, into one of which a test-tube was fitted by means of a cork, while the other communicated with a manometer. The test-tube reached to about the middle of the bottle, and its lower, closed, end was surrounded by a cylinder of phosphorus which was kept cool by a current of water, of the same temperature as the water-bath, which flowed through the test-tube. The whole apparatus stood in a large water-bath the temperature of which was kept constant. The experiments were made as follows:—The bottle, containing a little water and air, was placed in the thermostat, connected with the manometer, and allowed to stand until it had assumed the temperature of the bath. The phosphorus cylinder was then quickly placed in position and the pressure read off. Subsequent readings of the pressure made at convenient intervals furnished the data from which the velocity of the reaction was calculated. The concentration of the oxygen is proportional to its partial pressure so long as the volume remains constant (which was the case in the method just described), and the decrease of pressure per minute is proportional to the quantity of oxygen which undergoes change per minute—that is, to the velocity of the reaction.

The phosphorus was so little acted on during an experiment that its surface remained practically undiminished.

The numbers obtained in two experiments made in this way are given in the following Table (I.). They agree with those obtained by Ikeda in showing that the velocity of the reaction (in moist air) diminishes a little more slowly than the partial pressure of the oxygen. This is seen in the increase in the values of  $K'$  (column 4). These numbers are

\* Journ. Coll. Science, Imperial University, Japan, vi. p. 43 (1893).

calculated on the assumption that the rate of the reaction is proportional to the partial pressure of the oxygen. Or

$$-\frac{dp}{dt} = K'p. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

On integration this becomes

$$-\log p = K't + \text{const.}$$

We have  $p=p_0$ , when  $t=0$ ,  $p_0$  being the pressure of the oxygen at the beginning of the experiment.

We have, therefore,

$$\text{const.} = -\log p_0,$$

and

$$K' = \frac{1}{t} \log \frac{p_0}{p} \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

TABLE I.—Phosphorus and Moist Air.

Temperature = 20°·2 to 20°·4.				
Pressure of aqueous vapour . = 17·8 millim.				
,, phosphorus-vapour = 0·113 ,,				
Time, in minutes, from the beginning. <i>t</i> .	Total pressure. <i>P</i> .	Partial pressure of Oxygen = <i>p</i> .	<i>K'</i> .	<i>K</i> .
0	773·1	157·8		
25	750·6	135·3	·00267	42·0
50	729·7	114·0	·00282	43·1
75	714·3	99·0	·00271	40·1
100	697·4	82·1	·00284	42·3
130	682·2	66·9	·00286	42·1
Temperature = 20°·5 to 20°·68.				
Pressure of aqueous vapour . = 17·9 millim.				
,, phosphorus-vapour = 0·113 ,,				
0	764·6	156·0		
25	749·5	140·9	·00177	27·2
50	732·9	124·3	·00197	28·2
70	723·2	114·6	·00191	29·0
100	707·1	98·5	·00200	29·8
130	693·5	84·9	·00203	30·0
171	677·4	68·8	·00208	30·3
201	667·4	58·8	·00211	30·4
246	653·2	44·6	·00221	31·4

The vapour-pressure of phosphorus was determined by Joubert, *loc. cit.*



*Influence of the Rate of Evaporation.*

The fact that  $K'$  increases as the pressure falls shows that the reaction takes place somewhat faster at lower pressures than one would expect if its velocity were directly proportional to the pressure. This may be due to the fact that substances evaporate more rapidly into a gaseous atmosphere when its pressure is small than when it is larger. There can be little doubt that the reaction takes place between phosphorus-vapour and oxygen; and, furthermore, if it is allowable to take the phosphorescent light as an indication of the locality of the reaction, it takes place close to the surface of the phosphorus so long as the pressure of the oxygen is not very small\*. There are thus grounds for supposing that the phosphorus-vapour is oxidized as fast as it is evolved from the surface of the phosphorus, and therefore that the velocity with which the reaction goes forward will be directly proportional to the rate of evaporation of the phosphorus. By making this assumption, as we shall see, it is at any rate possible to give a coherent and fairly satisfactory account of reactions the courses of which would otherwise appear to be totally exceptional.

According to Stefan †, when all the other conditions remain constant, the rate of evaporation of a liquid into a gas is connected with the pressure of the latter by the following formula:—

$$v = c \log \frac{P}{P - p'};$$

where

$v$  = the rate of evaporation,

$P$  = total pressure of the gas and vapour,

$p'$  = the vapour-pressure of the liquid,

and  $c$  = some constant.

Introducing this correction for the changeable velocity of evaporation into equation (1), we obtain

$$-\frac{dp}{dt} = Kp \cdot \log \frac{P}{P - p'} \dots \dots \dots (2)$$

In order to integrate this equation we may write  $p = P - a$ , where  $a$  is the partial pressure of the nitrogen and aqueous vapour in the mixture of gases, and therefore constant. After making this substitution and expanding the logarithm,

\* The luminous phenomena accompanying the oxidation of phosphorus have been carefully described by v. Marum, *loc. cit.*; Joubert, *Thèses*, 1874; Fischer, *J. prakt. Chem.* xxxv. p. 343 (1845); Schrötter, *Sitzungsber. Wien. Akad.* ix. p. 414 (1852), and others.

† *Sitzungsber. K. Akad. d. Wiss. Wien*, lxxviii. 1878, p. 385.

the equation may be brought into the form

$$-Kdt = \frac{dP}{P-a} \left[ \frac{P}{p'} - \frac{1}{2} - \frac{1}{12} \frac{p'}{P} - \frac{1}{24} \frac{(p')^2}{P^2} - \&c. \right].$$

This can be easily integrated between the limits  $P_0$  and  $P$ , and gives:—

$$\begin{aligned} Kt = \frac{P_0 - P}{p'} + \left( \log \frac{P_0 - a}{P - a} \right) & \left[ \frac{a}{p'} - \frac{1}{2} - \frac{p'}{12a} - \frac{p'^2}{24a^2} - \&c. \right] \\ & + \left( \log \frac{P_0}{P} \right) \left[ \frac{p'}{12a} + \frac{p'^2}{24a^2} + \&c. \right] \\ & + \frac{p'^2}{24a} \cdot \frac{P_0 - P}{P_0 P} \&c. \quad \dots \dots \dots (2a) \end{aligned}$$

For phosphorus at ordinary temperatures,  $p'$  is so small compared with  $a$  that the equation may, without appreciable error, be written

$$Kt = \frac{P_0 - P}{p'} + \left( \log \frac{P_0 - a}{P - a} \right) \left[ \frac{a}{p'} - \frac{1}{2} \right] \quad \dots \dots (2b)$$

The values of  $K$  in the fifth column of Table I. have been calculated by means of this equation. The numbers are more nearly constant than those obtained by means of the uncorrected equation (1).

It appears, therefore, from these experiments that the velocity of the reaction is proportional to the pressure of the oxygen. This cannot be true at all pressures, however, for when the pressure of the oxygen is greater than a certain limit the velocity of the reaction becomes zero.

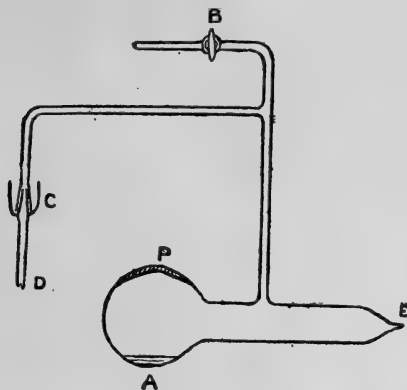
(b) *Phosphorus in Moist Oxygen. Behaviour at Higher Pressures.*

A further series of measurements was therefore made in which the whole range of pressures at which the reaction takes place was studied.

For this purpose a somewhat different form of apparatus was used. After various trials that shown in fig. 1 was found to be most convenient. The glass vessel E P A (50–70 cubic centim. capacity) was connected by means of a capillary tube ( $\frac{1}{2}$  millim. diameter) with the tap B and with the manometer D. The joint at C was usually made by means of a ground-glass joint luted with mercury; occasionally a thick indiarubber tube was used. The manometer was arranged so that the mercury always stood at the same height in the limb D, the volume of the apparatus therefore remained constant. A mercury-gauge was mostly used, but some of the experiments at lower pressures were made with a manometer

in which the mercury was replaced by bromnaphthalene. This allowed of a more accurate reading of the pressure, and the vapour of the bromnaphthalene did not appear to interfere in any way with the course of the reaction. The phosphorus was purified by melting it under a dilute solution of potassium bichromate and sulphuric acid, and carefully washing it.

Fig. 1.



A piece of this phosphorus was brought into the apparatus through E, melted at P, distributed in as thin a layer as possible over the upper surface of the bulb, and allowed to solidify in that position. This was generally done in an atmosphere of carbon dioxide, sometimes *in vacuo*. By this means as large a surface of the phosphorus as possible is exposed to the cooling action of the water in the bath in which the apparatus is plunged. The product of the oxidation also tends to fall and not to collect on the surface of the phosphorus. A little water was placed in the apparatus at A, and E sealed up before the blowpipe.

After placing the apparatus in position in the water-bath, it was evacuated as completely as possible and oxygen allowed to enter. This operation was repeated several times. A precaution which is of importance is to keep the phosphorus cold; otherwise, on allowing the oxygen to flow into the vacuous apparatus, it is very apt to take fire. This is especially the case when the oxygen is dry and the pressure is very low; with oxygen which had been dried by passing over phosphorous pentoxide I have even seen the spontaneous inflammation occur at  $0^{\circ}\text{C}$ . The pressure was probably less than that due to 1 millim. of mercury.

No attempt was made to measure the absolute velocity of the reaction, as this would have involved the accurate measurement of the area of the surface of the phosphorus. The constants obtained are therefore different in each experiment, The temperature varied irregularly between the limits given.

TABLE II.—Phosphorus and Oxygen.  
(Saturated with aqueous vapour.)

Temperature = $9^{\circ}\cdot 1$ to $9^{\circ}\cdot 2$ . Pressure of aqueous vapour . = $8\cdot 6$ millim. "      phosphorus-vapour = $0\cdot 046$ millim. "      nitrogen . . . = $3\cdot 4$ millim.			
Time in minutes from beginning = $t$ .	Total pressure in mm. of mercury. P.	Partial pressure of Oxygen. $p$ .	K. Calculated from equation 2b.
0	94.3	82.3	
83	43.7	31.7	16.2
96	38.4	26.4	15.7
124.5	27.1	15.1	15.3
152	21.2	9.2	14.2
169	18.0	6.0	13.9
195	14.7	2.7	13.4
236	13.1	1.1	12.2

Temperature = $20^{\circ}\cdot 2$ to $20^{\circ}\cdot 7$ Pressure of aqueous vapour . = $17\cdot 6$ to $18\cdot 2$ millim. "      phosphorus-vapour = $0\cdot 116$ millim.				
$t$ .	P.	Pressure of Nitrogen.	$p$ .	K.
0	750.7	37.5	695.6	
22	750.7	"	695.6	0.0
50	749.6	"	694.5	0.06
80	745.8	"	690.7	0.18
171	736.5	"	681.3	0.77
0	736.5	"	680.6	
255	671.0	"	615.3	2.39
0	601.6	33.4	549.9	
57	542.7	"	491.0	9.79
0	487.7	30.1	439.4	
30	457.2	"	408.9	9.86
0	397.8	26.2	353.4	
25	372.3	"	327.9	9.95

The pressure was artificially reduced from time to time by pumping out part of the gas. Old apparatus used in this experiment and in the next.

TABLE II.—Phosphorus and Oxygen (*continued*).

Temperature = 20°·43 to 20°·64.			
Pressure of aqueous vapour . = 17·9 millim.			
,, phosphorus-vapour = 0·116 millim.			
<i>t.</i>	P.	<i>p.</i>	K.
0	801·8	783·9	
79	801·8	783·9	
0	740·7	722·8	
52	741·9	724·0	
0	689·0	671·1	
43	684·2	666·3	0·99
0	615·9	598·0	
37·5	581·8	563·9	8·08
0	491·5	473·6	
24	463·3	445·4	10·52
0	340·2	322·3	
22·5	312·2	294·3	11·34
Temperature = 20°·18 to 20°·24.			
Pressure of aqueous vapour . = 17·6 millim.			
,, phosphorus-vapour = 0·111 millim.			
<i>t.</i>	P.	<i>p.</i>	K.
0	484·1	457·4	
17	420·8	394·1	35·6
0	252·5	225·8	
36·5	146·7	120·0	30·2
0	107·7	81·0	
15	65·7	39·0	36·4
40	32·3	5·6	26·3
60	26·7	0·0	26·6
Temperature = 20°·54 to 20°·6.			
Pressure of aqueous vapour . = 18·0 millim.			
,, phosphorus-vapour = 0·116 millim.			
,, nitrogen . . . = 6·6 millim.			
<i>t.</i>	P.	<i>p.</i>	K.
0	264·0	239·4	
21	200·2	175·6	29·3
40	150·5	125·9	27·9
50	124·0	99·4	27·9
64	90·0	65·4	27·8
84	50·0	25·4	27·8
104	30·8	6·2	27·0
124	25·3	0·7	26·8

TABLE II.—Phosphorus and Oxygen (*continued*).

Temperature = $29^{\circ}\cdot59$ to $29^{\circ}\cdot79$ . Pressure of aqueous vapour . = 31 millim. " phosphorus-vapour = $0\cdot25$ millim. " nitrogen . . . = 8 millim.			
<i>t.</i>	P.	<i>p.</i>	K.
0	230·0	191·0	
4·5	204·4	165·4	27·7
9·5	170·0	131·0	31·4
14·5	138·9	99·7	32·0
19·5	114·4	75·2	31·1
24·5	91·3	52·3	30·9
30·5	73·7	34·7	29·1
34·5	65·6	26·6	28·0
39·5	57·5	18·3	26·6
45·5	52·7	13·5	24·6
49·0	50·2	11·0	23·6
54·0	47·3	8·0	22·6

Temperature = $29^{\circ}\cdot15$ to $29^{\circ}\cdot3$ . Pressure of aqueous vapour . = $30\cdot1$ mm. mercury. " phosphorus-vapour = $0\cdot205$ mm. " " nitrogen . . . = $3\cdot02$ mm. " Bromnaphthalene manometer used. Sp. gr. of the bromnaphthalene was 1·5108 at ordinary temperature.			
<i>t.</i>	P in mm. of bromnaphthalene.	<i>p</i> in mm. of mercury.	K.
0	1210·0	101·0	
5	954·5	72·6	39·1
13	626·5	33·9	38·3
17	521·0	24·5	35·6
23	444·5	15·9	23·5
29·5	391·0	10·0	22·0
37	357·0	6·2	19·3
47	316·5	1·7	19·9
56	300·5	0·1	21·3
93	300·0	0	

Temperature = $29^{\circ}\cdot6$ to $29^{\circ}\cdot8$ . Pressure of aqueous vapour . = 281 mm. bromnaphthalene. " phosphorus-vapour = $2\cdot43$ mm. " " nitrogen . . . = $52\cdot2$ mm. " Bromnaphthalene manometer used.			
<i>t.</i>	P in mm. of bromnaphthalene.	<i>p</i> in mm. of mercury.	K.
0	1375·0	115·7	
4·5	1212·5	97·7	20·0
8·5	1049·5	79·6	21·8
12·5	887·0	61·5	22·9
18·5	684·0	38·9	23·4
27·0	597·0	29·3	18·8
46·0	532·5	22·1	12·4
106·0	476·5	15·9	6·0

TABLE II.—Phosphorus and Oxygen (*continued*).

Temperature = 30°·18 to 30°·31.			
Pressure of aqueous vapour .		= 288·9 mm. bromnaphth.	
,, phosphorus-vapour		= 2·36 mm. „	
,, nitrogen . . .		= 260·7 mm. „	
<i>t.</i>	P in millims. of bromnaphthalene.	<i>p</i> in millims. of mercury.	K.
0	1334·5	87·2	
4	1240·0	76·7	17·5
6	1197·0	70·9	17·2
9	1126·0	64·0	17·9
11	1081·0	59·0	18·0
13	1037·0	54·2	18·3
17	958·0	45·4	18·3
21	883·0	37·0	18·6
28·5	774·5	25·0	18·5
32·5	750·5	22·3	17·4
37·5	721·0	19·0	16·4
58·5	655·0	11·7	13·9
105·5	559·0	1·0	12·9

Determinations of the limiting pressure, above which no reaction takes place, were only made at 20°. In one experiment at 20°·2 (see Table II.) the reaction just began when the pressure of the oxygen was 696 millim. In another at 20°·5 it began at 671 millim., but not at 723 millim. We may therefore say that at a temperature of 20°–21° phosphorus will just begin to oxidize in wet oxygen when its pressure is about 700 millim.

Joubert\* gives two series of experiments on the pressure at which phosphorus just begins to be luminous in oxygen. At 20°·2, one series gave 787 millim., the other 666 millim. The pressure at which oxidation just begins appears, therefore, to be identical with that at which the phosphorescence just becomes visible.

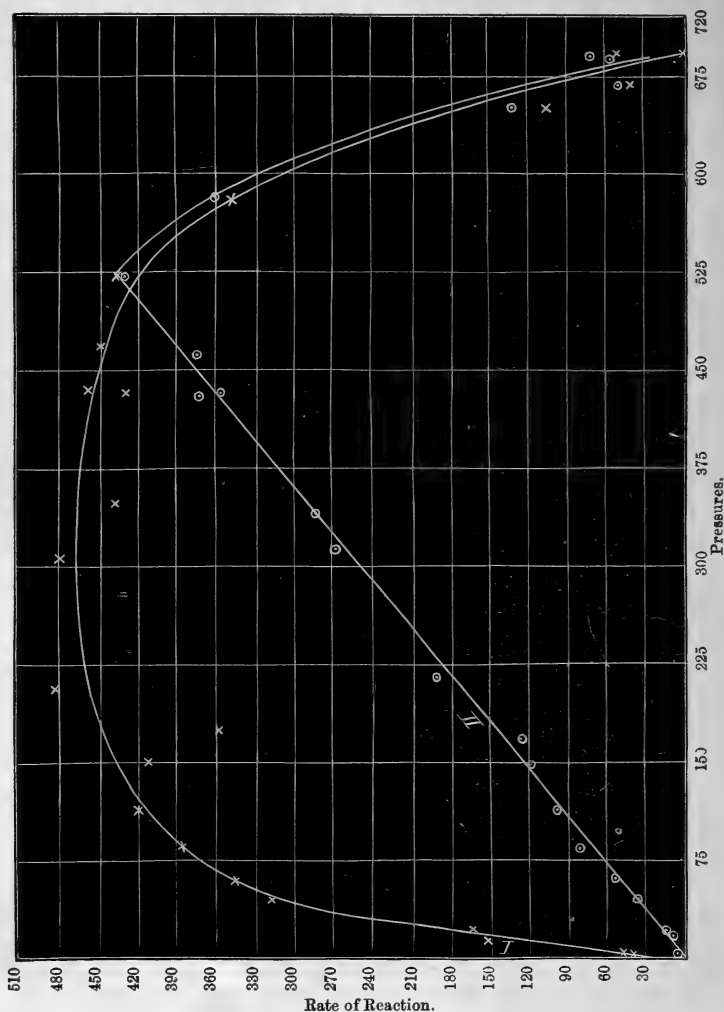
The curves in fig. 2 show the connexion between the pressure and the velocity of the reaction between phosphorus and wet oxygen. The experiments at 20° being the most complete have been used in drawing them. The values of the velocities of reaction have been obtained by dividing the successive decrements of the pressure by the corresponding increments of the time.

These values of  $\frac{\Delta p}{\Delta t}$  are taken as ordinates, and the mean

\* *Loc. cit.*

values of the partial pressure of oxygen in each interval as abscissæ. The actual numbers, which are easily calculated

Fig. 2.



from those given in Table II., are not included in that Table, in order to avoid unnecessary complication. A glance at



curve I. (fig. 2) will show that the velocity of the reaction beginning with the value 0 at 700 millim. increases at first very rapidly as the pressure falls, then varies between narrow limits over a considerable range of pressure (viz., from 500-100 millim.), and finally decreases again rapidly. Curve II.

(fig. 2) is obtained by dividing the values of  $\frac{\Delta p}{\Delta t}$  from which curve I. is constructed by the corresponding values of  $\log \frac{P}{P-p}$ , the rate of evaporation of the phosphorus. That is, it represents the rate at which the reaction would go forward if the rate of evaporation of the phosphorus were constant. The numbers so obtained (represented in the figure by circles) evidently lie on a straight line passing through the origin. That is, the *corrected* velocities are proportional to the partial pressures of the oxygen. This, however, is only true up to a pressure of about 520 millim. At higher pressures the curve changes its direction, and the velocity very quickly decreases to 0.

A more accurate way of testing the truth of this relationship is to be found in the calculation of the values of the constant K in equation 2 b. On looking over the numbers given in Table II., it will be seen that the values of K (at 20°) are approximately constant at pressures smaller than 550 millim. The numbers sometimes increase, sometimes decrease; the variations may therefore be ascribed to experimental error.

The same is true for the experiments made at 30°, for pressures between 200 and 25 millim. (no measurements were made at pressures greater than 200 millim.). Below 25 millim., however, there is always a marked decrease in the values of K, and traces of a similar behaviour are to be found in the experiments at 20°, and also in the one experiment at 9°. This diminution in the velocity of the reaction at low pressures may possibly have been due to the steam and nitrogen with which the oxygen was mixed hindering the interdiffusion of the oxygen and phosphorus-vapour.

We may conclude, therefore, that wet oxygen at ordinary temperatures acts on phosphorus with a velocity which may be represented by the equation

$$-\frac{dp}{dt} = K \cdot p \cdot \log \frac{P}{P-p}.$$

Above a certain limiting pressure (which probably varies with the temperature) this ceases to be true, the reaction taking place very much more slowly.

### PHOSPHORUS AND DRY OXYGEN.

Turning now to the action of dried oxygen on phosphorus quite a different result is obtained.

The experiments were made by the method and with the apparatus already described. The water in the glass vessel at A (fig. 1) was merely replaced by phosphorus pentoxide. In the first experiment the oxygen was allowed to remain in contact with the phosphorus pentoxide for a week, in the second, for two days. The numbers obtained are given in the following Table.

TABLE III.—Phosphorus and Dry Oxygen.

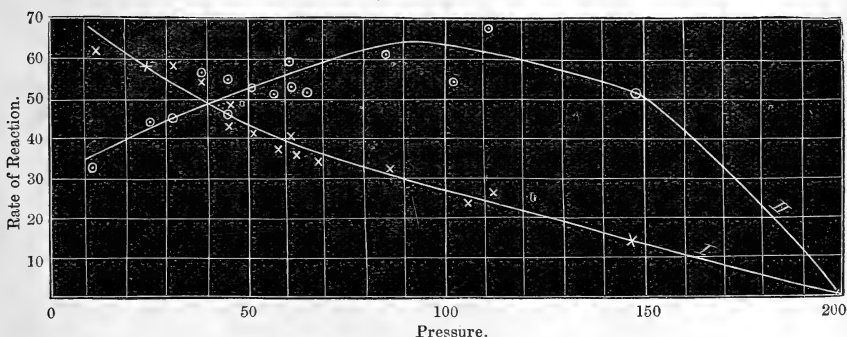
Temperature = $20^{\circ}\cdot87$ to $21^{\circ}\cdot26$ . Pressure of phosphorus-vapour = $0\cdot12$ millim.					
Time in minutes from the beginning. <i>t</i> .	Total pressure. P.	Partial pressure of Nitrogen. ( <i>a</i> ).	Partial pressure of Oxygen. <i>p</i> .	$K_1$ .	K.
0	433.5	56.5	377.0	1.23	
70	433.3				
0	231.9	30.3	201.6		
15	231.9		201.6		
55	231.5		201.2		
110	230.5		200.2		
0	122.0	16.0	106.0		
20	117.2		101.2	23.4	2.31
120	86.2		70.2	27.5	2.95
142	78.9		62.9	27.7	3.02
161	71.1		55.1	28.2	3.18
181.5	62.2		46.2	29.0	3.31
192	57.1		41.1	29.3	3.45
204	50.4		34.4	30.0	3.63
218	36.7		20.7	32.5	4.29
227	34.9		18.9	31.7	4.21
236	26.0		10.0	33.0	4.73
253.5	21.7		5.7	31.9	4.83

TABLE III.—Phosphorus and Dry Oxygen (*continued*).

Temperature = 20°.4 to 20°.65.					
Pressure of phosphorus-vapour = 1.035 mm. bromnaphth.					
<i>t.</i>	P. In millim. of brom- naphthalene.	<i>a.</i> In millim. of brom- naphthalene.	<i>p.</i> In millim. of mercury.	<i>K</i> <sub>1</sub> .	<i>K</i> .
0	1412.8	59.4	150.4		
18	1395.8	"	148.5	35.1	
35	1381.5	"	146.9	32.8	
0	1082.5	46.7	115.1		
31	1036.0	"	109.9	45.7	
45	1012.7	"	107.3	48.9	
0	608.0	28.0	64.4		
10	589.0	"	62.3	46.0	1.93
19	566.0	"	59.8	52.9	2.23
21.5	561.0	"	59.2	52.2	2.21
35	531.5	"	55.9	51.6	2.22
48.5	498.5	"	52.3	52.4	2.29
67	451.5	"	47.1	53.2	2.38
106	347.0	"	35.4	53.4	2.53
116	313.0	"	31.7	54.2	2.62
127.5	270.0	"	26.9	55.1	2.74

The reaction now first began at a much lower pressure than formerly. Under a pressure of oxygen of 377 millim. it did not begin ; it just began when the pressure was reduced to 202 millim. Curve I. (fig. 3) shows the connexion between

Fig. 3.—Phosphorus and Dry Oxygen.



the pressure of the oxygen and the velocity with which it acts on the phosphorus. The curve is constructed from the figures given in Table III. in the same way as before. Setting

out from the pressure of 200 millim., at which the velocity of the reaction is 0, it appears to increase continuously as the pressure falls, and not to reach a maximum value as is the case when the gas is moist. Curve II. (fig. 3) is obtained by dividing the values of the rate of reaction from which curve I. is drawn by the corresponding values of the rate of evaporation of the phosphorus, and plotting the numbers so obtained against the pressures. The numbers are so irregular that it is not easy to make out the true nature of the curve. The values of the ordinates of the part of the curve between 0 and 70 millim., however, appear to be proportional to the square roots of the corresponding values of the pressure.

We have, accordingly,

$$-\frac{dp}{dt} = K_1 p^{\frac{1}{2}} \log \frac{P}{P-p}, \quad \dots \dots (3)$$

which is the same equation as has already been found to hold good for phosphorus and moist oxygen, except that the velocity of the reaction is put proportional to the square root of the partial pressure of the oxygen instead of to the pressure itself.

This equation may be integrated by expanding the logarithm in the same way as before: this gives, neglecting small terms,

$$-K_1 t = \frac{2}{3p'} (P-a)^{\frac{3}{2}} + \left(\frac{2a}{p'} - 1\right) (P-a)^{\frac{5}{2}} + \text{const.}$$

The value of the constant is obtained from the condition that  $P = P_0$ , when  $t = 0$ ;  $P_0$  being the total pressure at the beginning of the experiment. Introducing the value of the constant, we obtain

$$K_1 t = \frac{2}{3p'} [(P_0 - a)^{\frac{3}{2}} - (P - a)^{\frac{3}{2}}] + \left(\frac{2a}{p'} - 1\right) [(P_0 - a)^{\frac{5}{2}} - (P - a)^{\frac{5}{2}}]. \quad (3a)$$

It is by means of this expression that the values of  $K_1$  given in Table III. have been calculated. The numbers show that  $K_1$  is approximately constant from a pressure of 60–70 millim. downwards; at higher pressures it diminishes. The irregularity of the numbers is probably due, in part at any rate, to the deposition of a coating of oxide on the surface of the phosphorus. We may therefore say that the rate of evaporation of the phosphorus being supposed constant, it is acted on by dry oxygen with a velocity which is proportional to the square root of its pressure. This is only true (at 20°) up to a pressure of some 60–70 millim.; above this pressure the velocity decreases. It is of interest that the greatest

velocity of the reaction occurs in this case at very nearly the same pressure as that which van't Hoff found to be most favourable to the reaction between phosphine and oxygen.

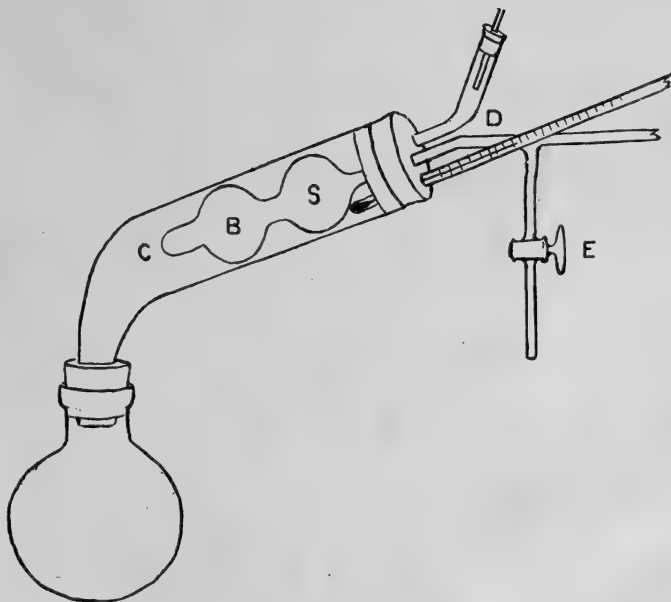
In Table III. the values of  $K$  calculated from equation (2 *b*) (in which the rate of reaction is put proportional to the pressure) are also given. They are much less constant than the values of  $K_1$ .

#### SULPHUR AND OXYGEN.

The course of this reaction is more regular than that of the last, because the products of oxidation being volatile the surface of the sulphur remains unchanged.

The first experiments were made by a method similar to that which was used with phosphorus, the volume being kept constant and the pressure allowed to change. The essential part of the apparatus is shown in fig. 4. It consisted of a

Fig. 4.



tube with two bulbs blown upon it, B, S, and of 60–70 cubic centim. capacity. At S, 1–2 grams of pure sulphur, at B, 5–6 grams of soda-lime were placed, and the end C sealed up before the blowpipe. The capillary-tube D connected the apparatus with a manometer, and with the tap E, by means of which it was filled with oxygen. The whole was heated

to a temperature of about  $160^{\circ}$  in the vapour of boiling turpentine. The following Table contains the results of an experiment made by this method.

TABLE IV.—Sulphur and Oxygen.

Temperature =  $156^{\circ}$ .

Vapour-pressure of sulphur = 11.5 millim.\*

Pressure of nitrogen . . = 8.1 millim.

Time in minutes from beginning. $t$ .	Total pressure. $P$ .	Partial pressure of Oxygen $= p$ .	$K_1$ .
0	132.5	114.0	
18	121.0	102.5	74
41	107.2	88.7	64
58	93.4	74.9	65
75	79.9	61.4	63
84	71.6	53.1	65
97	58.7	40.2	65
107	47.6	29.1	65
119	30.0	11.5	65
128	20.0	1.5	63

$K_1$  was calculated from the equation obtained by the integration of equation 3. Owing to the magnitude of  $p'$ , equation (3a) is insufficiently accurate, and two further terms of the expansion of the logarithm have to be included. The equation thus obtained is:—

$$\begin{aligned}
 -K_1 t = & \frac{2}{3p'}(P-a)^{\frac{3}{2}} + \left( \frac{2a}{p'} - 1 - \frac{p'^2}{24aP} \right) (P-a)^{\frac{1}{2}} \\
 & - \frac{p'}{6\sqrt{a}} \tan^{-1} \left( \frac{P-a}{a} \right)^{\frac{1}{2}} \\
 & - \frac{p'^2}{24a^{\frac{3}{2}}} \sin^{-1} \left( \frac{P-a}{P} \right)^{\frac{1}{2}} \\
 & + \text{const.}
 \end{aligned} \quad (3b)$$

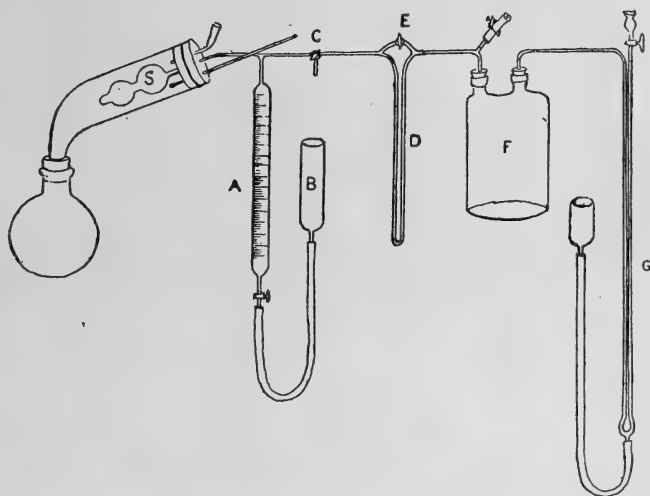
The integration-constant is determined as before. With the exception of the first number, the values of  $K_1$  are very satisfactorily constant; equation (3) therefore applies also to this reaction.

\* On further heating pressure remained constant at 18.5 millim.; after cooling pressure = 5.4 millim. at  $12^{\circ}$ . From which pressure of the sulphur-vapour = 10.4 millim. Another experiment gave 12.6 millim.

It was found that more satisfactory results could be obtained by using a different method, in which the pressure was kept constant and the diminution of volume measured. This method has the advantage that it allows several measurements of the velocity to be made at each pressure; by this means accidental variations can be eliminated. It was noticed, for example, almost invariably that at the beginning of an experiment (the pressure being constant) the rate at which the volume diminished was not constant. The reaction commenced too fast, and only reached a constant velocity after some time. This doubtless accounts for the abnormally large value of  $K_1$  at the beginning of the experiment in Table IV.

The apparatus finally adopted is shown in fig. 5.

Fig. 5.



The tube S containing the sulphur and oxygen remains unchanged. It was attached to a graduated tube A, containing mercury, the height of which could be changed by means of the reservoir B. C is a three-way tap; D a sensitive gauge containing bromnaphthalene, it serves to show when the pressure in the part of the apparatus to its left is equal to that in the reservoir F. The tap E serves to put the parts of the apparatus to the right and to the left of D in communication with each other when necessary. The reservoir F, which serves to keep the pressure constant, is in communication with the manometer G and with an air-pump.

The part of the apparatus to the left of D having been filled with oxygen at a somewhat greater pressure than exists in F, the tap E is opened for a moment to equalize the pressure on both sides of D, and the position of the mercury in A read off. By raising B the pressure of the oxygen can always be kept equal to the constant pressure in F. The diminution of volume per minute, when reduced to standard pressure, is then proportional to the velocity of the reaction. When the velocity has become constant, the pressure in F is reduced, the tap E opened to equalize the pressure again, and further readings made at the new pressure.

The following Table contains the numbers obtained by this method.

In it  $\frac{\Delta v}{\Delta t}$  is the diminution of the volume per minute, the volume being measured at pressure P.

$\frac{dv}{dt}$  is the rate of change of the volume, calculated for a pressure of 819.7 millim., and it is proportional to the quantity of oxygen which is converted into sulphur dioxide per minute, that is to the rate of the reaction.

TABLE V.—Sulphur and Oxygen.

Pressure. P.	$\frac{\Delta v}{\Delta t}$	$\frac{dv}{dt}$	Tempera- ture.	$K_2$	$k$ .
809.8	.0176	.0174	158	.0985	.0035
587.0	.0244	.0175	158	.0841	.0035
380.6	.0459	.0213	158	.0820	.0042
198.5	.147	.0356	159	.0975	.0069
105.6	.456	.0588	159	.118	.0156
43.8	1.77	.0946	159	.108	.0163
819.7	.0149	.0149	158	.085	.0030
578.7	.0243	.0172	159	.082	.0034
422.2	.0349	.0180	159	.088	.0043
306.0	.0653	.0244	159.5	.084	.0048
194.0	.133	.0315	159.2	.085	.0061
147.3	.222	.0399	"	.093	.0077
95.9	.455	.0532	159.4	.098	.0100
41.8	1.84	.0938	"	.104	.0161

The constant  $K_2$  is calculated from the following equation, which is essentially identical with equation 3:—

$$-\frac{dv}{dt} = K_2 P^{\frac{1}{2}} \log \frac{P}{P-p'}.$$



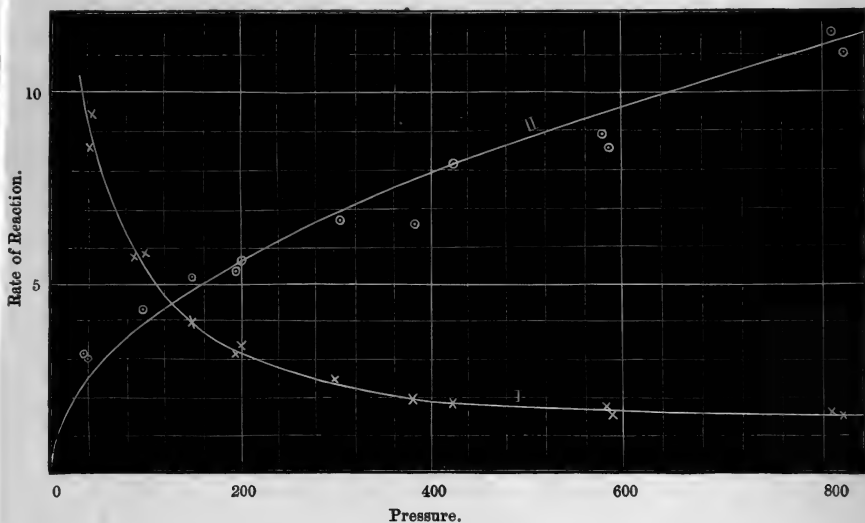
$k$  (Table V.) is calculated by the formula

$$-\frac{dv}{dt} = kP \log \frac{P}{P-p'}.$$

It is evident that the formula in which the velocity of the reaction is put proportional to the square root of the pressure is in much better agreement with the truth than that in which it is put proportional to the pressure itself.

The curves in fig. 6 represent the connexion between the

Fig. 6.—Sulphur and Oxygen.



velocity of the reaction and the pressure. Curve I. is drawn with the values of  $\frac{dv}{dt}$  as ordinates and pressures as abscissæ.

It has a strong general resemblance to the curve representing the velocity of the reaction between phosphorus and dry oxygen. The velocity continuously increases as the pressure falls. Curve II. is drawn with ordinates proportional to the square roots of the corresponding pressures. The experimental values of the velocity of the reaction corrected for the rate of evaporation of the sulphur, viz. :

$$\frac{dv}{dt} / \log \frac{P}{P-p'},$$

are represented in the figure by circles. The theoretical curve evidently represents these points with fair approximation.

It is interesting to notice that the whole curve here, up to 800 millim., corresponds to the part of the curve for phosphorus and dry oxygen between 0 and 70 millim. It would be of interest to make experiments with sulphur and oxygen at higher pressures in order to find out whether a maximum velocity occurs similar to that found with phosphorus.

#### ALDEHYDE AND OXYGEN.

When, as in the experiments which have just been described, the substance which is undergoing oxidation is a solid or a liquid, its rate of evaporation becomes such an important factor in determining the rate of the reaction, that it is not easy to make out with perfect certainty what rôle is played by the concentration of the oxygen. It appears, however, very probable that in dry oxygen the rate of the reaction is proportional to the square root of its concentration. In order to further test the truth of this result, experiments were made on the reaction between aldehyde-vapour and oxygen. The reaction was found to go on with convenient speed at  $20^{\circ}$ . As aldehyde boils at  $21^{\circ}$  under a pressure of 760 millim., it was assumed that aldehyde-vapour at  $20^{\circ}$  and under pressures not exceeding 550 millim. might be regarded with sufficient approximation as a perfect gas. Numerous attempts were made to absorb the acetic acid formed, by means of some solid substance without action on the aldehyde.  $\text{PbO}$ ,  $\text{ZnO}$ ,  $\text{BaCO}_3$ ,  $\text{KC}_2\text{H}_3\text{O}_2$  (anhydrous), were tried, but they all appeared to cause a more or less rapid diminution in the quantity of the aldehyde-vapour. The experiments were therefore made without any such absorbent.

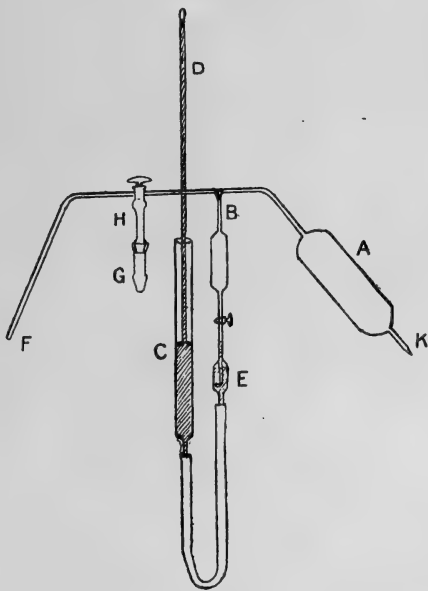
The apparatus used (fig. 7) was essentially the same as that which was employed by van't Hoff for the study of the formation of water from electrolytic gas (*Etudes de dyn. chimique*, p. 53), and for the study of the decomposition by heat of  $\text{PH}_3$  and  $\text{AsH}_3$ . The reaction takes place in the bulb A (fig. 7): this has a capacity of 60 to 70 cubic centim., and is immersed in a water-bath maintained at a constant temperature. The tubes connecting A to the rest of the apparatus, which are not plunged in the water, are made of capillary diameter in order to diminish as far as possible the volume of gas which is at the temperature of the air. The pressure of the gas in the apparatus is determined by means of the manometer B C D. By raising or lowering the tube C, the level of the mercury

was always brought to B before a reading was made. The pressure of the gas in the apparatus is then obtained by reading the difference in level between B and D: for this purpose a vertical millimetre-scale was generally used, sometimes a cathetometer.

C D is a barometer, the lower end of which just dips under the mercury at C. The air-trap at E is useful in preventing bubbles of air, which sometimes leak through the indiarubber tube, from passing back into the apparatus.

By means of the three-way tap H the apparatus can be connected either with an air-pump through F, or with a little vessel containing liquid aldehyde (G), which is ground to fit the lower limb of the tap. The apparatus having been

Fig. 7.



evacuated as completely as possible, the tap is turned so that the aldehyde-vapour distils into it. By repeating this operation several times, the air may be completely replaced by aldehyde-vapour at any desired pressure up to 500–600 millim. This having been done the tap H is closed, the apparatus put in position in the water-bath, and the pressure of the aldehyde-vapour observed. F is then connected with a tube delivering pure oxygen dried over  $\text{CaCl}_2$ , which is allowed to flow

through FH until it is full of oxygen. The tap H is then quickly opened, to admit the oxygen, closed again, and the pressure read off. Further readings are then made from time to time until the reaction is ended. The gases take some time to diffuse into each other, so that the velocity of the reaction was frequently rather small at the beginning.

The calculation of the experiments required a knowledge of the composition of the gas which remained in the apparatus at the end of the experiment. As soon as the last reading of the pressure had been made, therefore, a very dilute solution of caustic potash was allowed to flow into the apparatus from a weighed flask. The difference between the volume of the apparatus (determined by weighing it full of water) and the volume of the caustic-potash solution drawn into it, gave the volume of oxygen and nitrogen contained in the residue. Caustic potash was used in order to polymerize any aldehyde left.

The mixture of oxygen and nitrogen was then transferred to a graduated tube, and shaken with an alkaline solution of pyrogallol. The part which was left unabsorbed was taken to be nitrogen. The transference of the residual gas from the bulb A to the graduated tube was effected by running water in through the capillary tube K after breaking off its sealed end.

In many of the earlier experiments a comparatively large quantity of gas remained which was not absorbed by the solution of pyrogallol and caustic potash. It was noticed, however, finally that this gas was inflammable, and that its formation was accompanied by some action of the mixture of aldehyde and oxygen on the mercury in the manometer, a white substance, which was insoluble in water, being formed.

On protecting the mercury by placing a very small quantity of bromnaphthalene over its surface, no formation of the white substance occurred, and the gas which remained unacted upon by the pyrogallol was much smaller in quantity than formerly, and no longer inflammable. It is probable also that the reaction is accelerated by light. The following experiment may be quoted in support of this view. The temperature was  $19^{\circ}.98$  to  $20^{\circ}.07$ .

The constant K was calculated by means of equation (5), which was found to apply to this reaction. The value of the constant appears to be influenced by the brightness of the light. For this reason the experiments were finally made in the dark. It appears also to be of some importance to keep the apparatus as clean as possible. It was generally allowed

to remain over night filled with a solution of potassium permanganate and hydrochloric acid. The manganese dioxide formed was removed by means of oxalic acid; the apparatus was then well washed with distilled water and dried by a current of air.

Time.	Pressure of Oxygen. $p_1$ .	Pressure of Aldehyde. $p_2$ .	K.	Remarks.
11.26 A.M.	196.8	543.2	...	Cloudy.
11.50 "	182.0	510.2	0.76	"
12.21 P.M.	160.4	457.6	0.89	"
2.33 "	86.3	269.5	1.19	Direct sunlight
3.6 "	72.8	241.3	1.24	on apparatus.
3.56 "	57.5	211.2	1.27	
7.8 "	28.7	158.1	1.20	
8.17 "	23.7	149.1	1.08	Nearly dark.

The following Table contains the results of the experiments which were made with the precautions mentioned :—

TABLE VI.—Aldehyde and Oxygen.

Time in minutes from the beginning. $t$ .	Pressure of Oxygen. $p_1$ .	Pressure of Aldehyde. $p_2$ .	Total pressure. P.	$K \times 10^5$ .
0	225.8	536.0	785.0	
67	210.3	499.1	744.5	2.91
117	200.5	466.9	702.5	2.94
190	188.1	427.3	651.5	2.81
259	177.1	395.8	608.0	2.84
270	174.6	388.8	598.5	2.93
296	167.2	368.7	571.0	3.16
332	161.4	353.5	550.0	3.19
386	150.7	324.7	510.5	3.43
476	136.6	292.3	464.0	3.57
673	118.3	251.6	405.0	3.40
1303	83.8	183.1	302.0	3.29

Temperature =  $20^{\circ}.1$  to  $20^{\circ}.32$ .

Partial pressure of oxygen at the end of experiment = 83.4 millim.

Partial pressure of nitrogen at the end of experiment = 23.7 "

Total pressure at the end of the experiment . . . = 301 "

Vapour-pressure of acetic acid at  $20^{\circ}.2$  . . . = 11.4 "

$k' = 0.002873$ .

Table VI. (continued).

Time in minutes from the beginning. <i>t.</i>	Pressure of Oxygen. <i>p</i> <sub>1</sub> .	Pressure of Aldehyde. <i>p</i> <sub>2</sub> .	Total pressure. <i>P.</i>	<i>K</i> × 10 <sup>5</sup> .
0	489.6	291.2	799.0	
72	485.3	281.7	790.5	0.96
98	480.6	273.2	781.0	1.52
132	475.5	251.2	766.5	1.81
163	470.0	249.2	749.0	2.05
229	457.2	220.5	707.5	2.87
325	441.6	186.1	657.5	2.94
464	424.2	159.5	603.5	3.11
617	409.1	119.1	558.0	3.18
1330	376.5	57.2	463.5	3.00

Temperature = 20°·5 to 20°·7.

Total pressure of residual gas . . . . . = 473.5 millim.

Partial pressure of residual oxygen . . . . . = 376.5 "

Partial pressure of residual nitrogen . . . . . = 18.2 "

Vapour-pressure of acetic acid at 20°·6 . . . . . = 11.6 "

*k'* = 0.00103.

<i>t.</i>	<i>p</i> <sub>1</sub> .	<i>p</i> <sub>2</sub> .	<i>P.</i>	<i>K</i> × 10 <sup>5</sup> .
0	595.7	270.0	878.0	
146	.....	.....	878.0	
0	533.2	241.6	785.7	
136	532.3	239.9	783.1	
1163	532.3	239.7	782.9	
0	373.0	178.5	559.3	
353	346.8	122.8	488.8	2.82
421	344.6	118.2	481.8	2.59
501	342.7	114.2	476.1	2.34

Temperature = 20°·8.

Total pressure at end of experiment . . . . . = 442.6 millim.

Partial pressure of oxygen at end of experiment . . . . . = 331.9 "

Partial pressure of nitrogen at end of experiment . . . . . = 7.8 "

*k'* = 0.001767.

Another experiment at 21°·4 gave no reaction when the pressure of the oxygen was 599 millim., and also when it was reduced to 530 millim. the reaction did not begin.

The calculation of the amount of change which had occurred at any moment, from the change of pressure, is complicated by the solvent action of the liquid acetic acid formed on the aldehyde-vapour : owing to this the amount of change at any

given moment is not simply proportional to the diminution of the pressure.

Suppose that at the commencement of the experiment, the partial pressure of the aldehyde were  $=a$  millim., that of the oxygen  $=b$  millim., and that of the nitrogen  $=N$  millim. And let  $P$  be the total pressure of the gas at any time,  $t$  minutes after the beginning of the experiment. Suppose also that at the same instant  $x$  millim. of oxygen have united with  $2x$  millim. of aldehyde. At first the acetic acid formed remains as vapour, and as its density at  $20^\circ$  is double the normal value, we shall have 2 volumes of aldehyde-vapour and 1 volume of oxygen condensing to form 1 volume of acetic-acid vapour. That is, the acetic-acid vapour will occupy the same volume and exert the same pressure as the oxygen from which it is formed; and the pressure of the mixture will be

$$P = (a - 2x) + (b - x) + x + N \\ = a + b - 2x + N.$$

The pressure at the beginning of the experiment ( $P_0$ ) was equal to  $a + b + N$ , so that we obtain

$$2x = P_0 - P.$$

After a time the acetic-acid vapour will reach its maximum pressure (say  $m$ ), after which liquid acetic acid will be formed, and its quantity will be proportional to  $(x - m)$ , that is  $=k(x - m)$ . If we assume that the quantity of aldehyde dissolved in the acetic acid follows Henry's law, it will be proportional to the pressure of the gaseous aldehyde and to the quantity of liquid acetic acid; that is, to  $k'(x - m)p_2$ , where  $p_2$  is the pressure of the aldehyde-vapour.

The pressure of the aldehyde-vapour at any moment is its original pressure diminished by the part which has undergone chemical reaction and by the part dissolved in the acetic acid; that is

$$p_2 = a - 2x - k'(x - m)p_2,$$

or

$$p_2 = \frac{a - 2x}{1 + k'(x - m)}. \quad \dots \dots \dots (4)$$

It may be pointed out that even if the assumption that aldehyde-vapour dissolved in acetic acid follows Henry's law is not strictly accurate, no great error will be committed, because the quantity dissolved is not large.

We also have the equation expressing the total pressure  $P$

as the sum of the pressures of oxygen  $(b-x)$ , aldehyde  $p_2$ , acetic-acid vapour  $m$ , and nitrogen  $N$ , viz.:—

$$P = (b-x) + p_2 + m + N.$$

Substituting the value of  $p_2$  just found, we get

$$P = (b-x) + \frac{a-2x}{1+k'(x-m)} + m + N.$$

From this equation  $x$  (the diminution in the oxygen pressure) may be obtained when  $k'$  is known. The analysis of the gas at the end of an experiment gives a direct determination of  $x$  from which  $k'$  may be found. The expression is unfortunately a quadratic in  $x$ , and is best solved by successive approximations, which, however, makes the calculations somewhat laborious.

The connexion between the velocity with which oxygen and aldehyde-vapour unite to form acetic acid and the concentration of the gases (or their partial pressures, which are proportional to the concentrations) is expressed by the equation

$$-\frac{dp_1}{dt} = K \cdot \sqrt{p_1} \cdot p_2 \cdot \dots \dots \dots (5)$$

$p_1$  = the partial pressure of the oxygen,  $p_2$  that of the aldehyde.

$-\frac{dp_1}{dt}$  is the rate at which the pressure of the oxygen diminishes.

To integrate this equation substitute (from equation 4)

$$p_2 = \frac{a-2x}{1+k'(x-m)},$$

$$p_1 = (b-x),$$

and

$$-\frac{dp_1}{dt} = \frac{dx}{dt}.$$

This gives

$$\frac{dx}{dt} = K \cdot (b-x)^{\frac{1}{2}} \cdot \left( \frac{a-2x}{1+k'(x-m)} \right).$$

After performing the integration this becomes

$$Kt = \frac{2lm - k'a - 2}{4 \left( \frac{2b-a}{2} \right)^{\frac{1}{2}}} \log \frac{(b-x)^{\frac{1}{2}} - \left( \frac{2b-a}{2} \right)}{(b-x)^{\frac{1}{2}} + \left( \frac{2b-a}{2} \right)} + k'(b-x)^{\frac{1}{2}} + \text{const.} \quad (5a)$$



The constant is obtained from the condition that  $x=0$ , when  $t=0$ .

This form of the integrated equation can only be used when  $(2b-a)$  is positive, because its square root occurs in the expression. For the case that excess of aldehyde is present at the commencement of the experiment, and  $(2b-a)$  therefore negative, the integrated equation may be brought into the following form:—

$$Kt = \frac{2k'm - 2 - k'a}{2\left(\frac{a-2b}{2}\right)^{\frac{1}{2}}} \tan^{-1} \frac{(b-x)^{\frac{1}{2}}}{\left(\frac{a-2b}{2}\right)^{\frac{1}{2}}} + k'(b-x)^{\frac{1}{2}} + \text{const.} \quad (5b)$$

The values of  $K$  in Table VI. are calculated by means of equations (5a) and (5b), and show that up to a pressure of 450 millim. these equations are in harmony with the experimental results.

When the partial pressure of the oxygen is higher than about 450 millim., however, the values of  $K$  decrease. This points to the existence of an upper limit of pressure, above which the reaction either stops altogether or goes forward with a velocity very much smaller than that which would be deduced from equation 5.

As a matter of fact, in the two last experiments given in Table VI. no reaction occurred when the pressure of the oxygen exceeded 530 millim. Further experiments are, however, needed in order to put this very interesting behaviour beyond doubt.

We may say, therefore, that oxygen and aldehyde-vapour react with formation of acetic acid with a velocity which is proportional to the pressure of the aldehyde-vapour and to the square root of the pressure of the oxygen. It is possible that a pressure of oxygen exists above which this is no longer true. At 20° this pressure appears to be that due to about 450 millim. of mercury.

#### INTERPRETATION OF RESULTS.

Following van't Hoff\*, the velocity of a reaction of the general form



that is of one in which  $m$  molecules of a substance A react with  $n$  molecules of B, &c., to form  $p$ ,  $q$ , &c. molecules of the new substances C, D, &c., may be written

$$-\frac{dC_1}{dt} = k \cdot C_A^m \cdot C_B^n \dots \dots \dots (6)$$

\* *Etudes de Dynamique Chimique.*

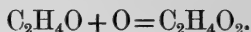
$-\frac{dC_1}{dt}$  is the rate at which the system  $A_1B_1\dots$  changes into the other system  $C_1D_1\dots$   $C_1$  is the concentration of the first system,  $C_A, C_B, \&c.$  the concentrations of the substances  $A, B\dots$

In cases in which the numbers of molecules taking part in a reaction are unknown, measurements of the velocity of the reaction may be made use of for their determination.

Applying this to the reaction between aldehyde and oxygen, we have  $-\frac{dC_1}{dt}$  in equation 6 proportional to  $-\frac{dp}{dt}$  in equation 5.  $C_A$  we may put proportional to the pressure of the aldehyde-vapour, and  $C_B$  to the pressure of the oxygen gas. Making these substitutions in 6, we get

$$-\frac{dp_1}{dt} = \text{const. } p_2^m \cdot p_1^n,$$

and comparing this with 5, we see that  $m=1$  and  $n=\frac{1}{2}$ . The reaction between aldehyde and oxygen may therefore be written



We must suppose that the reaction consists in the addition of an oxygen atom to a molecule of aldehyde.

The assumption that a certain small number of oxygen atoms exist normally in oxygen gas, is in accordance with our present knowledge on the subject. Williamson was led by his studies on the formation of ethers to propose the theory that the atoms of which the molecules of a gas are composed frequently change partners. For this to be possible, a certain number of atoms must be at any moment in the act of transition, that is free. The theory of Clausius, based on the phenomena of electrolytic conductivity, and more recently that of Arrhenius, supposes a similar condition to exist in solutions of electrolytes. In 1884 J. J. Thomson \* developed a mathematical theory of chemical reactions between gases, based on the ideas of Williamson and Clausius; the results are in agreement with those obtained experimentally with aldehyde and oxygen.

The probability of the existence of free atoms in oxygen gas may be shown in another way. There can be little doubt, from analogy, that the oxygen molecule would, at a sufficiently high temperature, be dissociated into its atoms. Equilibrium will be established when the concentration of the atoms has reached a certain value which is determined by the equation

$$C_{(O_2)} = kC_{(O)}^2,$$

where  $C_{(O_2)}$  is the concentration of the oxygen molecules and

\* Phil. Mag. [5] xviii. p. 233 (1884).

$C_{(O)}$  that of the atoms.  $k$  is a constant which depends on the temperature\*. As the heat of formation of the oxygen molecule from its atoms is probably positive, the equilibrium will change with falling temperature, in such a way that the concentration of the oxygen atoms will diminish. It will, however, probably never become nothing. If this be true at ordinary temperatures, we shall have

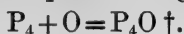
$$C_{(O)} = \text{const.} \sqrt{C_{(O_2)}}.$$

As the concentration of the oxygen atoms is small, we can put the concentration of the oxygen molecules proportional to the pressure of the gas, and the concentration of the oxygen atoms will then be proportional to the square root of the pressure of oxygen. If we assume, therefore, that the atoms alone take part in the oxidation of the aldehyde, we shall have the velocity of the reaction always proportional to the square root of the pressure of the oxygen.

Although the results of the experiments with aldehyde admit of such a simple interpretation, it is doubtful whether this is also the case with those obtained with phosphorus and sulphur.

We should expect the connexion between the velocity of the reaction and the concentration of the oxygen to be less simple than that actually found.

Possibly in the case of sulphur and phosphorus with dry oxygen the reaction takes place in stages; for example,



The velocity of the whole reaction would then be the sum of the velocities of the part reactions, each one of which would be proportional to the concentration of the oxygen atoms. This view is also in agreement with the fact that when phosphorus is burnt with a limited supply of oxygen, the lower oxides, such as  $P_4O_6$ , are formed.

The fact that the presence of moisture accelerates the oxidation of phosphorus‡ and sulphur is also in accordance with the view that the oxidation is due to the presence of oxygen atoms; for Professor J. J. Thomson§ has found that it is

\* See van't Hoff, *Etudes*, p. 127.

† The existence of this oxide, discovered by Le Verrier, is rendered probable by the work of Reinizer and Goldschmidt (*Berl. Ber.* xiii. p. 845, 1880).

‡ In very dry oxygen phosphorus apparently does not oxidize at all. (H. B. Baker, *Phil. Trans.* 1888, p. 571.) Unfortunately Baker does not mention particularly the pressure under which the oxygen stood. Sulphur still burns in extremely dry oxygen, but with much greater difficulty than when the gas is moist. (Baker; and also Dewar, *Proc. Roy. Soc.* January 1893.)

§ J. J. Thomson, British Association, Oxford Meeting, 1894.

much more easy to cause an electric discharge (without electrodes) to pass through moist oxygen than through the gas when it is dry. The moisture apparently favours the formation of the atoms which carry the discharge. It must be confessed, however, that this view does not explain the formation of ozone which accompanies the oxidation of phosphorus, not only in moist oxygen but also, according to Marchand\*, in the dry gas.

The complicated nature of the reaction which takes place when phosphorus is oxidized in presence of water makes it impossible to do more than guess at an interpretation of the results obtained. Perhaps, however, the different nature of the equation representing the connexion between the velocity of the reaction and the pressure of the oxygen is due to the water taking part in the reaction.

The interesting fact that a pressure of oxygen exists at which the oxidation has a maximum velocity in the case of phosphorus, and perhaps also in that of aldehyde, requires further investigation before any satisfactory attempt can be made to account for it.

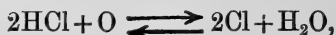
In conclusion it is perhaps worth noticing that, in one or two other cases which have been studied by other observers, the results are in harmony with the theory of Williamson.

Le Châtelier† has shown, using the results of Hautefeuille and Margottet, that, at constant temperature, the equilibrium which occurs when chlorine, hydrogen, and oxygen are exploded together can be represented by the expression

$$\log \frac{p_{(O_2)} \times p_{(HCl)}^4}{p_{(Cl_2)}^2 \times p_{(H_2O)}^2} = \text{const.},$$

in which  $p_{(O_2)}$ ,  $p_{(HCl)}$ ... are the partial pressures in the equilibrium of the oxygen, hydrochloric acid,....

If we suppose the reaction to occur between dissociated molecules we may write the reaction which occurs as follows:—



which would correspond to the equation

$$\log \frac{p_{(O_2)}^{\frac{1}{2}} \times p_{(HCl)}^2}{p_{(Cl_2)} \times p_{(H_2O)}} = \frac{\text{const.}}{2},$$

which is the equation given by Le Châtelier after dividing both sides by 2.

In conclusion, my best thanks are due to Prof. van't Hoff, in whose laboratory the foregoing work was done, for his advice and assistance during its progress.

\* *Journ. prakt. Chem.* **1**, p. 1 (1850).

† *Comptes Rendus*, **cix.** p. 665 (1889).

LXII. *On the Expressibility of a Determinant in Terms of its Coaxial Minors.* By THOMAS MUIR, LL.D.\*

1. **I**N a memoir on "A certain Class of Generating Functions in the Theory of Numbers," recently published in the Philosophical Transactions†, Major MacMahon, F.R.S., establishes the following noteworthy theorem:—

*In the case of every determinant of even order greater than the second there are two special relations between its coaxial minors, and each of these two relations can be thrown into a form which exhibits the determinant as an irrational function of its coaxial minors: in the case of a determinant of odd order, on the other hand, no such relations exist, and it is not possible to express the determinant as a function of its coaxial minors.*

He deduces the theorem readily from another to the effect that—

*There are  $2^n - n^2 + n - 2$  relations between the coaxial minors of any determinant of the  $n^{\text{th}}$  order.*

His proof of this latter theorem, however, is not by any means simple, occupying as many as eight pages (pp. 133–140) of the memoir. By reason of the importance of the theorem a simpler proof is much to be desired, and part of my object at present is to supply the want.

2. I start from the familiar proposition, that if the rows of a determinant of the  $n^{\text{th}}$  order be multiplied by  $x_1, x_2, x_3, \dots, x_n$  respectively, and the columns be then divided by the same quantities, the determinant is unaltered in value; but I prefer to include it in a more general but equally evident theorem, viz.:—

*If the rows of a determinant of the  $n^{\text{th}}$  order be multiplied by  $x_1, x_2, x_3, \dots, x_n$  respectively, and the columns be then divided by  $x_1, x_2, x_3, \dots, x_n$  respectively, the determinant is unaltered in value, and each of the minors of the transformed determinant is, to a factor près, equal to the corresponding minor of the original determinant, the connecting multiplier being  $x_h x_k x_l \dots / x_r x_s x_t \dots$  if the minor belong to the  $h^{\text{th}}, k^{\text{th}}, l^{\text{th}}, \dots$  rows, and  $r^{\text{th}}, s^{\text{th}}, t^{\text{th}}, \dots$  columns of the original.*

From this we have manifestly the corollary:—

*The connecting multiplier in the case of the coaxial minors, as in the case of the whole determinant, is 1: in other words, the coaxial minors remain unaltered by the transformation.*

\* Communicated by the Author.

† Vol. clxxxv. (1894) pp. 111–160.

Next it is clear that

$x_1, x_2, x_3, \dots, x_n$  may be so chosen that all the elements of any one of the rows or columns, except the diagonal element, shall be 1.

For example, the first row,

$$a_{11}, \quad a_{12} \frac{x_1}{x_2}, \quad a_{13} \frac{x_1}{x_3}, \quad \dots, \quad a_{1n} \frac{x_1}{x_n}$$

may be made to take the form

$$a_{11}, \quad 1, \quad 1, \quad \dots, \quad 1$$

by giving  $x_1, x_2, x_3, \dots, x_n$  the values  $1, a_{12}, a_{13}, \dots, a_{1n}$  respectively.

It follows, therefore, that

Any determinant of the  $n^{\text{th}}$  order may be transformed so as to have 1 for  $n-1$  of its elements, and yet the determinant itself and all its coaxial minors remain unaltered in value.

3. This is the same as saying that  $2^n - 1$  quantities, viz. the determinant and its coaxial minors, can be expressed in terms of  $n^2 - (n-1)$  others, viz. the modified elements, which are not equal to unity. Eliminating the latter, and we have  $2^n - n^2 + n - 2$  relations connecting the former—and this is Major MacMahon's auxiliary theorem.

4. The proof leaves no doubt as to the existence of two relations between any determinant, when of even order higher than the second, and its coaxial minors: but it is worth while to intensify the conviction by putting the relations actually in evidence for a particular determinant. Perhaps the determinant which lends itself most easily to the end in view is

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & a & b \\ 1 & \frac{1}{a} & 1 & c \\ 1 & \frac{1}{b} & \frac{1}{c} & 1 \end{vmatrix}.$$

Here the four coaxial minors of the 3rd order are

$$\begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & a \\ 1 & \frac{1}{a} & 1 \end{vmatrix}, \quad \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & b \\ 1 & \frac{1}{b} & 1 \end{vmatrix}, \quad \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & c \\ 1 & \frac{1}{c} & 1 \end{vmatrix}, \quad \begin{vmatrix} 1 & a & b \\ \frac{1}{a} & 1 & c \\ \frac{1}{b} & \frac{1}{c} & 1 \end{vmatrix}.$$

Calling these A, B, C, D respectively, and denoting the original determinant by  $\Delta$ , we have the five relations

$$\left. \begin{aligned} A &= a - 2 + \frac{1}{a}, \\ B &= b - 2 + \frac{1}{b}, \\ C &= c - 2 + \frac{1}{c}, \\ D &= \frac{ac}{b} - 2 + \frac{b}{ac}, \\ \Delta &= \frac{(1-a)(1-b)(1-c)(ac-b)}{abc}. \end{aligned} \right\}$$

Clearly from these  $a, b, c$  may be eliminated, and five relations found, viz. connecting  $\overline{ABCD}$ ,  $\overline{ABCD\Delta}$ ,  $\overline{ABD\Delta}$ ,  $\overline{ACD\Delta}$ ,  $\overline{BCD\Delta}$ : manifestly, however, only two of the relations can be independent.

5. To find the simplest of the five, viz. that which connects  $\overline{ABCD}$ , let us call the two values of  $a$  in the first equation  $\alpha$  and  $\frac{1}{\alpha}$ , the two values of  $b$  in the second equation  $\beta$  and  $\frac{1}{\beta}$ , the two values of  $c$  in the third equation  $\gamma$  and  $\frac{1}{\gamma}$ , and let us substitute these values in the fourth equation. The eliminant is thus seen to be

$$\begin{aligned} &\left\{ \frac{\beta}{\alpha\gamma} - (2+D) + \frac{\alpha\gamma}{\beta} \right\} \left\{ \frac{\beta\gamma}{\alpha} - (2+D) + \frac{\alpha}{\beta\gamma} \right\} \left\{ \alpha\beta\gamma - (2+D) + \frac{1}{\alpha\beta\gamma} \right\} \\ &\left\{ \frac{\alpha\beta}{\gamma} - (2+D) + \frac{\gamma}{\alpha\beta} \right\} \left\{ \frac{1}{\alpha\beta\gamma} - (2+D) + \alpha\beta\gamma \right\} \left\{ \frac{\gamma}{\alpha\beta} - (2+D) + \frac{\alpha\beta}{\gamma} \right\} \\ &\left\{ \frac{\alpha\gamma}{\beta} - (2+D) + \frac{\beta}{\alpha\gamma} \right\} \left\{ \frac{\alpha}{\beta\gamma} - (2+D) + \frac{\beta\gamma}{\alpha} \right\} = 0; \end{aligned}$$

that is,

$$\begin{aligned} &\left\{ D+2 - \left( \frac{\alpha}{\beta\gamma} + \frac{\beta\gamma}{\alpha} \right) \right\}^2 \left\{ D+2 - \left( \frac{\beta}{\gamma\alpha} + \frac{\gamma\alpha}{\beta} \right) \right\}^2 \\ &\left\{ D+2 - \left( \frac{\gamma}{\alpha\beta} + \frac{\alpha\beta}{\gamma} \right) \right\}^2 \left\{ D+2 - \left( \alpha\beta\gamma + \frac{1}{\alpha\beta\gamma} \right) \right\}^2 = 0 \end{aligned}$$

or

$$\begin{aligned}
& (D+2)^4 \\
& - (D+2)^3 \left\{ \frac{\alpha}{\beta\gamma} + \frac{\beta\gamma}{\alpha} + \frac{\beta}{\gamma\alpha} + \frac{\gamma\alpha}{\beta} + \frac{\gamma}{\alpha\beta} + \frac{\alpha\beta}{\gamma} + \alpha\beta\gamma + \frac{1}{\alpha\beta\gamma} \right\} \\
& + (D+2)^2 \left\{ \frac{\alpha^2}{\beta^2} + \frac{\beta^2}{\gamma^2} + \frac{\gamma^2}{\alpha^2} + \beta^2\gamma^2 + \gamma^2\alpha^2 + \alpha^2\beta^2 \right. \\
& \quad + \frac{\beta^2}{\alpha^2} + \frac{\gamma^2}{\beta^2} + \frac{\alpha^2}{\gamma^2} + \frac{1}{\beta^2\gamma^2} + \frac{1}{\gamma^2\alpha^2} + \frac{1}{\alpha^2\beta^2} \\
& \quad \left. + 2\left(\alpha^2 + \beta^2 + \gamma^2 + \frac{1}{\alpha^2} + \frac{1}{\beta^2} + \frac{1}{\gamma^2}\right) \right\} \\
& - (D+2) \left\{ \frac{\alpha}{\beta\gamma} + \frac{\beta\gamma}{\alpha} + \frac{\beta}{\gamma\alpha} + \frac{\gamma\alpha}{\beta} + \frac{\gamma}{\alpha\beta} + \frac{\alpha\beta}{\gamma} + \alpha\beta\gamma + \frac{1}{\alpha\beta\gamma} \right. \\
& \quad + \sum \frac{\beta\gamma}{\alpha^3} + \sum \frac{\beta^3\gamma}{\alpha} + \sum \alpha^3\beta\gamma \\
& \quad + \sum \frac{\alpha^3}{\beta\gamma} + \sum \frac{\alpha}{\beta^3\gamma} + \sum \frac{1}{\alpha^3\beta\gamma} \left. \right\} \\
& + \left\{ \sum \alpha^4 + \sum \frac{\alpha^2\beta^2}{\gamma^2} + \alpha^2\beta^2\gamma^2 + 1 \right. \\
& \quad \left. + \sum \frac{1}{\alpha^4} + \sum \frac{\gamma^2}{\alpha^2\beta^2} + \frac{1}{\alpha^2\beta^2\gamma^2} + 1 \right\} = 0.
\end{aligned}$$

By utilizing the facts that

$$\alpha + \frac{1}{\alpha} = A+2, \quad \beta + \frac{1}{\beta} = B+2, \quad \gamma + \frac{1}{\gamma} = C+2,$$

this is readily transformed into

$$\begin{aligned}
& (D+2)^4 \\
& - (D+2)^3 (A+2)(B+2)(C+2) \\
& + (D+2)^2 \{ \Sigma (A+2)^2 (B+2)^2 - 2 \Sigma (A+2)^2 \} \\
& - (D+2) \{ \Sigma (A+2)^3 (B+2)(C+2) - 8(A+2)(B+2)(C+2) \} \\
& + \{ \Sigma (A+2)^4 - 2 \Sigma (A+2)^2 (B+2)^2 \\
& \quad + (A+2)(B+2)^2 (C+2)^2 \} = 0;
\end{aligned}$$

and by applying the  $\Sigma$  to the *four* letters A, B, C, D, it becomes

$$\begin{aligned}
& \{ (A+2)^4 + \Sigma (A+2)^2 (B+2)^2 (C+2)^2 + 8(A+2)(B+2)(C+2)(D+2) \\
& \quad - \Sigma (A+2)^3 (B+2)(C+2)(D+2) - 2 \Sigma (A+2)^2 (B+2)^2 = 0
\end{aligned}$$



An alternative form is got by performing the multiplications and rearranging. It is

$$\begin{aligned} &\Sigma A^2B^2C^2 - 2\Sigma A^3BC - \Sigma A^3BCD + 4\Sigma A^2B^2C - 6\Sigma A^2BCD \\ &\quad + \Sigma A^4 - 4\Sigma A^3B + 4\Sigma A^2BC + 6\Sigma A^2B^2 - 40ABCD = 0. \end{aligned}$$

The symmetry with respect to A, B, C, D is evident *à priori*.

Mowbray Hall, near Capetown, S.A.,  
September 5, 1894.

LXIII. *A Mode of Calculating a Limit to the Direct Effect of Great Eccentricity of the Earth's Orbit on Terrestrial Temperatures, showing the Inadequacy of the Astronomical Theory of Ice Ages and Genial Ages.* By EDWARD P. CULVERWELL, M.A., Fellow of Trinity College, Dublin\*.

THE fundamental assumption made by Dr. James Croll in his well-known writings on the Glacial Periods, and subsequently adopted by Sir Robert S. Ball in 'The Cause of an Ice Age,' is that we may attain to some approximate idea of the lowering of terrestrial temperatures, due to greater winter distance from the sun, by the following considerations:—

Were it not for solar heat the earth would sink to what Ball calls its natural zero, which must be nearly the absolute zero of temperature. Hence the effect of the sun-heat is to maintain it at its present excess above that temperature, and any decrease in sun-heat will be accompanied by a more or less proportionate decrease in the excess of the earth's temperature above the natural zero. To be on the safe side, however, Croll takes this natural zero as a temperature of  $-239^{\circ}$  F. (Pouillet's temperature of space), and Ball as  $-300^{\circ}$  F. Croll, in chap. xix. of 'Climate and Time,' which he devotes to this subject, supposes the midwinter temperature in an epoch of great eccentricity to be proportional to the sun-heat received on midwinter day—a supposition open to the obvious criticism that the adjustment of temperature to sun-heat can hardly be instantaneous. This is probably the reason why Ball modified the argument and takes the average winter temperature as proportional to the average daily winter heat from equinox to equinox.

I shall show, by actual comparison with terrestrial temperatures, that this assumption of the proportion between the

\* Communicated by the Author.

temperature at a place and the sun-heat received is utterly wide of the mark; but first I will endeavour to trace the origin of Croll's mistake. In 1830 Herschel wrote a paper "On the Astronomical causes which may influence Geological Phenomena," and in it he dealt with the possible changes of terrestrial temperature due to changes in the earth's minor axis, making use of the argument that a small percentage alteration above the absolute zero (which he says some place at  $-1000^{\circ}$  F., some at  $-5000^{\circ}$  F., and some lower still) due to a small percentage change in the annual quantity of sun-heat received would produce all the great change in temperature required by geologists. In such a case the method is perfectly valid, except that terrestrial radiation should not be taken as simply proportional to absolute temperature. In the centuries during which the earth receives less annual heat from the sun we may fairly suppose that a practically permanent state is reached in which the heat annually received by the globe as a whole is equal to that radiated by the globe as a whole. In that case we cannot complain of Herschel in 1830 treating the radiation as proportional to the temperature, and then treating the percentage decrease in temperature of the globe as a whole as equal to the percentage decrease in sun-heat received. Had he taken the law of cooling as at present stated—*i. e.* radiation varies as the fourth power of absolute temperature—the percentage decrease in temperature would (for small changes) only be one fourth of the percentage decrease in heat received. Subsequently Herschel, in a rather confused paragraph in his 'Outlines,' 369*a*, referred to by Croll (p. 37) as his authority, appears to apply the same method to calculating temperature differences between the northern and southern hemispheres in the period of great eccentricity. But he rejects the calculation immediately after on the ground that loss of heat in winter, through greater distance from the sun, is compensated for by greater duration of winter. Hence the paragraph does not really seem to justify Croll's application. For Croll applies the method to the temperature of limited portions of the earth's surface, in which, owing to the fact that heat is continually being transferred from one region to another, there is never a time at which the gain by sun-heat is equal to the loss by radiation.

The statement just made shows that for Croll's argument to have any practical validity as a method of calculating the winter temperatures in the epoch of great eccentricity, it is necessary not only that the temperature adjustments shall be made with great rapidity but also that the direct effect of

sun-heat on terrestrial temperatures in the latitudes with which glaciation is concerned shall be great compared with that of the heat transferred from latitude to latitude by air and ocean currents. That this is not the case in regard to the changes of temperature from summer to winter, we have a ready means of showing; indeed it appears that the direct effect of winter sun-heat in northern latitudes is but a trifling factor in keeping the temperature above the "natural zero" when compared with the heat transferred from place to place. For consider the equator: it receives nearly the same daily sun-heat during winter and summer, and its temperature stands continuously about  $380^{\circ}$  F. above Ball's "natural zero." Hence, if we calculate and then plot on a diagram the average daily summer and winter sun-heats for each latitude, on such a scale that the equatorial sun-heat is represented by 380, then the ordinates giving the summer and winter sun-heats for the different latitudes should also, if Herschel's principle were applicable, give the summer and winter excesses of their temperatures above the natural zero. In fig. 1 this has been done for latitudes  $40^{\circ}$  to  $90^{\circ}$ , the only ones we are concerned with in dealing with the Glacial Period. I have also shown by the dotted lines the mean of the 'Challenger's' January and July temperatures for the meridians  $90^{\circ}$  E. and  $90^{\circ}$  W. passing through the middle of the great Asiatic and American continents up to latitude  $70^{\circ}$ , beyond which reliable information cannot be obtained. The scale of sun-heat is shown at the left side, and the scale of Fahrenheit temperatures at the right of the centre line. By examining the figure we see that even in the Continental areas, where the most extreme variations are observed, the midwinter temperatures bear no relation whatever to the very small amount of winter sun-heat; so that we infer that the transference of heat from one latitude to another is the chief factor in winter temperatures.

If we were to follow Croll's method, and take the midsummer and midwinter sun-heats instead of the daily average, the discrepancy shown in the figure between actual temperatures and sun-heats would be enormously increased.

To complete the criticism, let us examine the most extreme of all climates, that of Yakutsh in Siberia. Here the midsummer temperature rises to about  $370^{\circ}$  over the "natural zero" and the midwinter sinks to  $260^{\circ}$ . But the daily average sun-heat in summer is to the daily average in winter as 1300 is to 260, or as 370 is to 74. Hence if the midwinter temperature be right, the midsummer ought to be  $1000^{\circ}$  F., or if the midsummer be right, the midwinter ought

to be  $-226^{\circ}\text{F}$ . If, following Croll's method, we calculate the midsummer and midwinter sun-heats, we find the ratio to be 7600 to 260, or 370 to 12.5. It is unnecessary to dwell on the discrepancy between these figures and the temperatures.

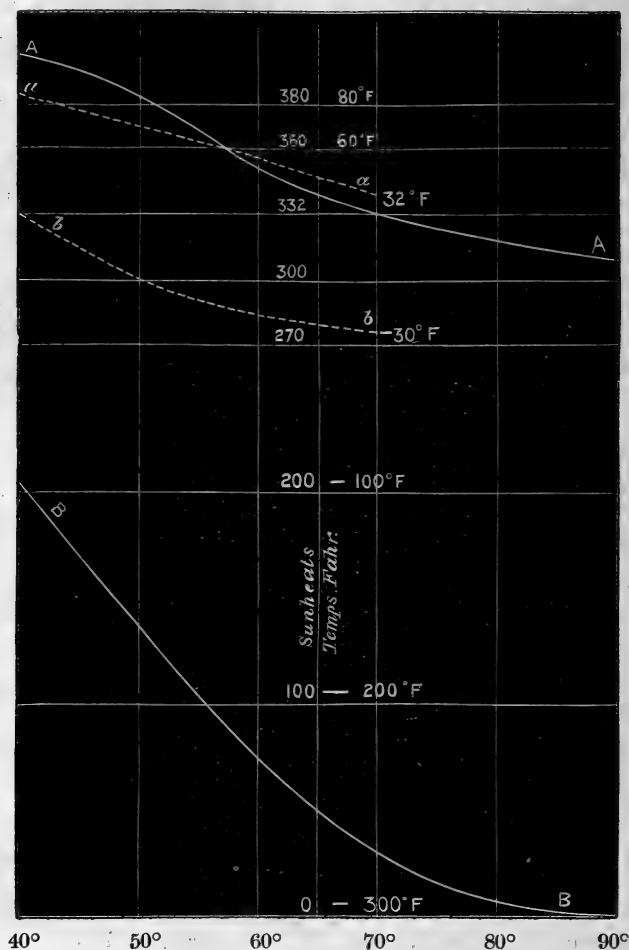


Fig. 1.—Showing the want of proportionality between winter temperatures and winter sun-heat.

A A, curve of average daily summer sun-heat.

B B, curve of average daily winter sun-heat.

a a, curve of mean Continental July temperatures.

b b, curve of mean Continental January temperatures.

When, therefore, there is such a complete absence of proportion between the summer and winter temperatures and the summer and winter sun-heats, what ground can be assigned for the assumption of a rough proportion between the *changes* in the summer or winter temperatures and the *changes* in the corresponding sun-heats due to eccentricity? Even if the temperatures themselves did show a certain rough proportion to the sun-heats, we could not expect as near an approach to the proportion in their *changes*, because the disturbing element might be large compared to the *changes* in the temperatures, though small compared to the temperatures themselves. As it is, the argument breaks down completely; and the assumption on which the supporters of the Astronomical theory of the Ice Ages and Genial Ages rely is found to be nothing but a vague speculation, not only unsupported by the physical evidence bearing on the subject, but in direct opposition to it. The weakness of the foundation, however, has not deterred the astronomical geologists from erecting on it an edifice of vast proportions. They affirm that there have been a number of successive glaciations, alternating with genial ages at intervals of about 10,500 years, that glaciation must have been simultaneous all round the pole, that a glacial age in the northern hemisphere must have been accompanied by a genial one in the southern, and *vice versâ*. And as M. Leverrier's calculations show that the last period of considerable eccentricity was about 100,000 years ago, the last Ice Age must have occurred about that date. Dr. Croll indeed fixes all the possible dates for three million years of past and one million of future time; but Sir Robert Ball declines to fix the dates, not from any want of implicit confidence in the theory, but merely from a probable want of accuracy in the determination of the astronomical constants involved. I imagine, however, that Sir Robert Ball would accept as fairly reliable Leverrier's calculations for this comparatively short period, though he does not accept those of Croll for the longer period. Hence we may safely assume with Croll, that the last Ice Age must have terminated 80,000 years ago, if his theory be correct.

When Croll's theory was originally published, the general opinion of geologists was that the date of the Ice Age as fixed by the theory was far too recent. But the uniformitarian school of those days has now been replaced by the modern school, which, relying on calculations of the rate of denudation, tends to fix the glaciation of North America as hardly more than ten or twenty thousand years ago. Hence geologists are now disposed to welcome any criticism of

Croll's hypothesis which tends to leave more freedom to the somewhat fluctuating demands of their science.

Is there, then, any physical method of estimating the changes in midwinter temperature due to eccentricity? The problem is of course far too complicated to be rigorously solved; but happily, in respect of the *direct* effect of sun-heat, we have what seems a fair and rational method of calculation. When, in the long winter of the supposed glacial epoch, the earth was much farther from the sun than at present, each parallel of latitude of course received less daily winter heat than the same parallel now receives. But let us find what parallels of latitude now receive the same sun-heat in winter as the parallels  $40^{\circ}$ ,  $50^{\circ}$ ,  $60^{\circ}$ ,  $70^{\circ}$ ,  $80^{\circ}$ , and the pole,  $90^{\circ}$ , which I will call the standard parallels, received in the long winter of great eccentricity. I take three bases of comparison—

*First*, following Croll's method, I find that *latitudes  $43^{\circ}$ ,  $52^{\circ}$ ,  $61^{\circ}$ ,  $70^{\circ}$ ,  $80^{\circ}$ , and  $90^{\circ}$  receive on midwinter day at present the same sun-heat as the standard latitudes received on their midwinter day in the period of great eccentricity.*

Now as to the temperatures. I think it is evident that the present midwinter temperatures of  $43^{\circ}$ ,  $52^{\circ}$ , &c. must, so far as direct sun-heat is concerned, be somewhat higher than those of the standard latitudes in the former epoch. For though the midwinter sun-heat is the same, the standard latitudes have had a longer period of cooling, *i. e.* the radiation from them in the earlier epoch has exceeded the sun-heat received for a few days longer than in the case of latitudes  $43^{\circ}$ ,  $52^{\circ}$ , &c. at present.

*Second.* I find that *latitudes  $43^{\circ} \cdot 3$ ,  $52^{\circ} \cdot 4$ ,  $61^{\circ} \cdot 7$ ,  $71^{\circ} \cdot 3$ ,  $81^{\circ}$ , and  $90^{\circ}$  now receive in their winter of 179 days just the same daily average of sun-heat as the standard latitudes received in their supposed glacial winter of 199 days.*

In this case, though the period over which the daily supply is taken is shorter in the case of  $43^{\circ} \cdot 3$ ,  $52^{\circ} \cdot 4$ , &c. than for the standard latitudes, yet the former *receive appreciably more midwinter sun-heat* than the latter; so that whatever difference of temperature there is due to the first cause will be more or less counterbalanced by the other, and we are probably not far wrong in saying that, so far as direct sun-heat is concerned, the present midwinter temperatures of latitudes  $43^{\circ} \cdot 3$ ,  $52^{\circ} \cdot 4$ ,  $61^{\circ} \cdot 7$ ,  $71^{\circ} \cdot 3$ ,  $81^{\circ}$ , and  $90^{\circ}$  must be about the same as those of  $40^{\circ}$ ,  $50^{\circ}$ ,  $60^{\circ}$ ,  $70^{\circ}$ ,  $80^{\circ}$ , and  $90^{\circ}$  were in the epoch of great eccentricity.

*Third.* I find that *latitudes  $44^{\circ} \cdot 2$ ,  $54^{\circ}$ ,  $63^{\circ} \cdot 5$ ,  $74^{\circ}$ , and  $84^{\circ} \cdot 5$  now receive the same total sun-heat in the 199 coldest days*

of our year as the corresponding standard latitudes received in the 199 coldest days of their year in the epoch of great eccentricity, that is, of course, in their winter (of course  $90^{\circ}$  cannot be brought into this comparison). In other words, *the same daily average of sun-heat is received during the 199 days by the corresponding latitudes in the present and former epochs.*

But it is quite evident that the present midwinter temperatures of  $44^{\circ}2$ ,  $54^{\circ}$ , &c. must, so far as the direct effect of sun-heat is concerned, be lower than the midwinter temperatures of the standard latitudes in the epoch of great eccentricity. For if the actual daily sun-heat received by latitude  $44^{\circ}2$  at present were the same for *each* of the 199 days as that received on the corresponding day by latitude  $40^{\circ}$  in the former epoch, then we could affirm that, so far as sun-heat alone was concerned, the temperatures of the two latitudes ought to be equal. But since  $44^{\circ}2$  receives far more than this amount of daily heat in the beginning of the 199 days, its temperature will be higher at first, and therefore, since the total heat received up to midwinter is the same in both cases, the temperature of the  $44^{\circ}2$  must be lower at midwinter—otherwise it would be higher all the time, which is impossible. For if it were higher all the time, it would be constantly losing more heat by radiation; wherefore, as it only receives the same quantity of heat, its final temperature must be lower, not higher. Thus the supposition that the midwinter temperature of  $44^{\circ}2$ , so far as direct sun-heat is concerned, is higher than that of  $40^{\circ}$  in the epoch of great eccentricity, involves an absurdity.

So far I have only dealt with the effect of the *winter* sun-heat. Consider now the *annual* sun-heat. First, the present summer sun-heat on lat.  $44^{\circ}2$  in the remaining 166 days of our year is far less (9 *per cent.* less) than the sun-heat received by lat.  $40^{\circ}$  in its summer of 166 days in the period of great eccentricity. Hence, so far as summer sun-heat is concerned, latitude  $44^{\circ}2$  now begins its 199 days at an appreciably lower temperature than  $40^{\circ}$  began its 199 days in the former epoch, and therefore, on this account as well, its present midwinter temperature should be lower than the midwinter temperature of  $40^{\circ}$  was in the supposed glacial winter.

Of course all the foregoing applies equally to the other latitudes.

Hence we conclude that, other things equal, the *direct* effect of the altered sun-heat in the epoch of great eccentricity was probably to place latitudes  $40^{\circ}$ ,  $50^{\circ}$ ,  $60^{\circ}$ ,  $70^{\circ}$ , and  $80^{\circ}$  in about the same conditions as to midwinter temperature as  $43^{\circ}3$ ,  $52^{\circ}4$ ,  $61^{\circ}7$ ,  $71^{\circ}3$ , and  $81^{\circ}$  are at present, and that

certainly the effect was not to lower their midwinter temperature to those of  $44^{\circ}20'$ ,  $54^{\circ}$ ,  $63^{\circ}5'$ ,  $74^{\circ}$ , and  $84^{\circ}5'$ , at the present time.

Next as to the *transference* of heat. Consider the latitudes from Cornwall to the Shetland Isles, *i. e.*  $50^{\circ}$  to  $60^{\circ}$ . In all probability the daily winter transference of equatorial heat to latitude  $50^{\circ}$  in the period of great eccentricity was greater than that to latitude  $54^{\circ}$  at present. For there is no doubt that the greater proportion of the transference is due to ocean currents. Now the experiments of the Prince of Monaco on the rate of motion of the Gulf Stream show that between the Azores and Ireland, and between Ireland and Norway, it is about 3.9 miles per day, or say 10 degrees in the half year. Hence *the winter heating of the British Isles by means of the Gulf Stream must depend very largely on the daily summer heat at a point about 10 degrees off on the path of the Gulf Stream, and this was much greater during the period of greatest eccentricity than now.* For it is easy to see by an examination of fig. 2 that during the 166 days of that short summer, latitude  $50^{\circ}$  received more heat than is now received in an equal time by any latitude, even in the tropics, while  $60^{\circ}$  received as much as  $52^{\circ}$  now receives,  $70^{\circ}$  as much as  $59^{\circ}$ , and  $80^{\circ}$  as much as  $66^{\circ}$  now receives. Thus when we remember how important a factor in winter temperature the heat transferred by ocean currents is, it might be plausibly maintained that the winter temperatures of the higher latitudes were probably higher in the supposed Glacial epoch than they are at present. But as the data are insufficient for obtaining a quantitative result by such arguments, it is better to be content with the extreme temperature limit, as fixed by the third method. This is obtained as follows:—

As we go northwards from latitude  $50^{\circ}$  to latitude  $70^{\circ}$  along the meridian of Greenwich we get a fall of  $15^{\circ}$  Fahr. in the midwinter temperature. Hence in that longitude the midwinter temperatures of latitudes  $54^{\circ}$ ,  $63^{\circ}5'$ , and  $74^{\circ}$  are about  $3^{\circ}$  Fahr. lower than those of  $50^{\circ}$ ,  $60^{\circ}$ , and  $70^{\circ}$ . Hence the fall of temperature in the epoch of greatest eccentricity cannot have been as much as  $3^{\circ}$  Fahr. in Great Britain, so far as the direct effect of sun-heat is concerned.

In mid-America and mid-Asia the change is somewhat greater. Taking the mean as we go northward from lat.  $50^{\circ}$  to lat.  $70^{\circ}$  along the meridians  $90^{\circ}$  W. long. and  $90^{\circ}$  E. long., we find that the midwinter temperature falls by  $1\frac{1}{4}^{\circ}$  Fahr. for each degree of latitude passed over to the northward. This would give a lowering of midwinter temperature of about  $5^{\circ}$  Fahr. for the 4 degrees of latitude by which the isothermals are shifted in the epoch of greatest eccentricity.



If, instead of taking the epoch of greatest eccentricity, we take the epoch of considerable eccentricity which occurred about 100,000 years ago, as calculated by Leverrier, we must take off about one fourth part from the above results.

Since the whole of Croll's theory of the stoppage of the Gulf Stream depends on a *previous* vast cooling of the northern hemisphere (accompanied by a heating of the southern hemisphere), it is evident that, unless the temperature results here given be utterly erroneous, they dispose once and for all of the Astronomical theory of the Ice Age. I have, however, prepared a further examination of that theory for the 'Geological Magazine' of January 1895.

With regard to the Genial Age, the insignificance of the changes effected by the astronomical cause is still more remarkable. When the eccentricity is at its maximum, and the winter occurs in perihelion, it will be seen from the figure that the winter isothermals are shifted  $2\frac{1}{2}$  or 3 degrees to the north and the summer ones about 5 degrees to the south. For instance, in our coldest 166 days lat.  $57^{\circ}5'$  receives just the same sun-heat as lat.  $60^{\circ}$  in the 166 days of the "genial" winter. To dwell on the inadequacy of this as the cause of the prevalence of tropical vegetation in Greenland and Spitzbergen would be mere loss of time. But Croll has an additional cause to account for a really Genial Age at the pole, namely, increased obliquity of the ecliptic. The maximum effect of this would be to increase by about  $\frac{1}{18}$  part the *summer* sun-heat received at the Poles. Hence, having said that  $\frac{1}{18}$  more ice would be melted annually at the Poles than at present, Croll proceeds to state that "the effects of eccentricity and obliquity thus combined" [*i. e.*, the maximum obliquity synchronizing with the "genial" conditions of the orbit] "would probably completely remove the polar ice-cap from off the latter hemisphere [that enjoying the "genial" conditions] and forest trees might then grow at the Pole."—'Climate and Time,' 2nd edition, pp. 402–403. It is as easy to make such assertions as this as it is difficult to adduce any shadow of a reason in support of them. That Croll should have been the person to make the astounding statement that the addition of  $\frac{1}{18}$  part of the *summer* heat at the Poles would prevent ice forming there during the winter is the more extraordinary, because in order to get over the difficulty that the summer heat in the supposed glacial epoch was just as much increased as the winter heat was diminished, it was necessary for him, throughout the earlier portion of his book, to insist on the absolute inefficiency of summer heat to melt ice and snow or to mitigate the effects of winter cold (see pp. 58–66 and p. 324 of 'Climate and Time'). So far, then, as

this suggestion of an additional cause of the Genial Age may require an answer, I leave Dr. Croll's earlier pages to answer his later ones.

The mode in which the calculations were made must now be explained. Originally I had intended to evaluate the integrals which give the winter sun-heat on each latitude, but the calculations appeared so long that I thought of using a graphic method by photographing a terrestrial globe in various positions. But having met with Mr. Meech's paper in vol. ix. of the 'Smithsonian Contributions to Knowledge,' I used his values for the daily heat on each 15th day of the year for intervals of 10 degrees of latitude as sufficiently close approximations to the quantities of sun-heat received on that day and the seven preceding and succeeding days, except in a few cases where the rate of change varied considerably, when I used a graphic method of interpolation by plotting the curve on millimetre-paper. Thus I was able to get the total quantity of sun-heat received (*a*) for winter and summer, using the words in their technical sense of the intervals between the equinoxes; (*b*) for our coldest 199 days; and (*c*) for our coldest 166 days, these being the lengths of the supposed glacial and genial winters. Of course, since the total annual sun-heat on any latitude is independent of the length of the seasons, it was easy to get the summer sun-heats for our 166 and 199 hottest days from these figures.

For the purposes of this paper I reduced the numerical values I had obtained from Mr. Meech's tables, so that the quantity of winter or summer sun-heat falling on the equator should be represented by 380, that being the excess of temperature of the equator above Ball's "natural zero." The numbers thus obtained are:—

Latitudes.....	40°	50°	60°	70°	80°	90°
Summer sun-heat .....	399	379	347	329	317	306
Winter sun-heat .....	199	138	79	32	7	0
„ coldest 199 days ...	229	161	101	48	16	5
„ coldest 166 days ...	179	121	66	23	3	0

I have plotted these numbers to scale in fig. 2.

The "summer" and "winter" sun-heats are of course the same whatever be the relative lengths of those seasons. Hence the shift of the isothermals is shown by lengths of the intercepts made by the sun-heat curves in fig. 2 on a horizontal line. The actual amount of the shift of the winter isothermals in the supposed Glacial epoch, as obtained from this figure, is, 40° to 44°·2, 50° to 54°, 60° to 63°·5, 70° to 74°, and 80° to

84°.5. These are practically identical with the result of the larger figure I originally made.

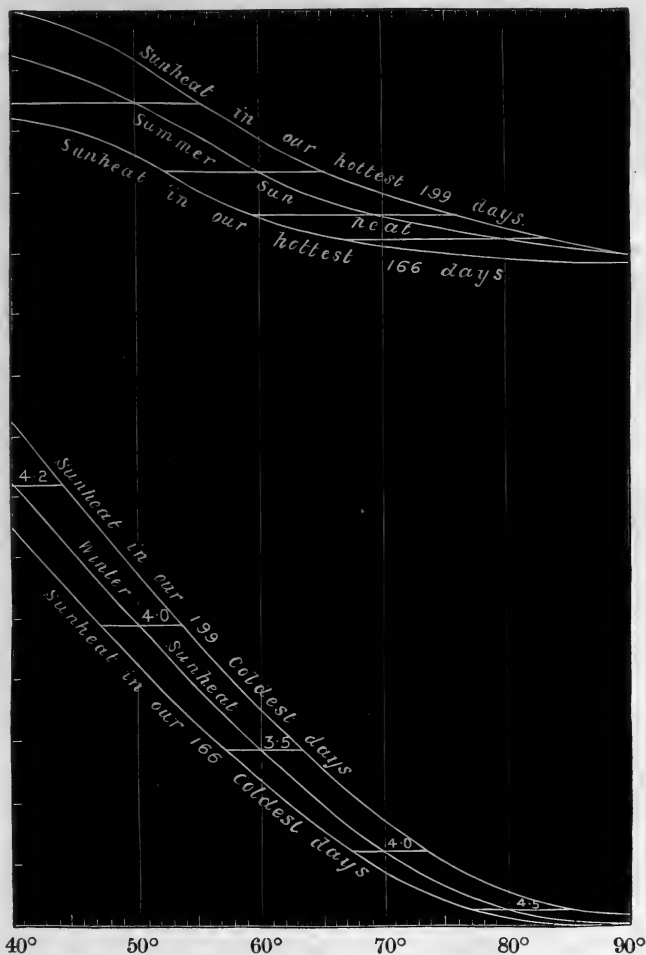


Fig. 2.—Showing the shift of the isothermals in the epoch of great eccentricity, as calculated by the third method.

There is one, and, as far as I can see, only one, objection that can be made to the results I have obtained. It might be urged that the winter heat at present received by lat. 54° from ocean currents is much in excess of that received in the epoch of great eccentricity by lat. 50°, and that therefore lat. 54° at present may be much warmer than lat. 50° was in the earlier epoch. The observations already made on

ocean currents seem a sufficient answer, but happily the objection can be entirely disposed of. For the transference of heat from ocean currents to lat.  $54^{\circ}$  at present depends on the excess of temperature of the ocean over what I may call the sun-heat temperature of  $54^{\circ}$ . Hence the objection supposes that the present midwinter excess of ocean temperature at  $54^{\circ}$  over the sun-heat temperature at  $54^{\circ}$  is greater than the excess of ocean temperature at  $50^{\circ}$  over the sun-heat temperature at  $50^{\circ}$  was in the epoch of great eccentricity. But since the present midwinter sun-heat temperature at  $54^{\circ}$  is the same as that at  $50^{\circ}$  in the earlier epoch, this supposition requires the midwinter ocean temperature to be now higher at lat.  $54^{\circ}$  than it was at lat.  $50^{\circ}$  in the epoch of great eccentricity. But since the sun-heat temperature of the ocean at lat.  $50^{\circ}$  at the earlier epoch was the same as that at lat.  $54^{\circ}$  now, there is nothing which could tend to make the winter temperature of the ocean at  $50^{\circ}$  in the earlier epoch lower than that at  $54^{\circ}$  now, while the far greater summer heating the water then underwent in the lower latitudes must have made its winter temperature higher than it is now. Hence the supposition that the winter temperature of the ocean would be lower is disposed of for Great Britain at least\*.

Of course the foregoing argument proceeds on the supposition that the configuration of the land, and with it the general character of the ocean currents and air currents was the same at the epoch of great eccentricity as it is now. It then supplies a satisfactory proof that there is nothing in the astronomical causes which would alter those currents, or at least nothing of the nature required by Croll's theory.

If, instead of taking the radiation proportional to the absolute temperature, we take Stefan's law, published in 1881, giving it as proportional to the 4th power of the temperature, we should reduce Croll's result by one fourth. Thus his  $45^{\circ} \cdot 3$  F. would come down to  $11^{\circ}$  F.; and if we further consider that ocean and air currents are twice as effective as winter sun-heat in maintaining the temperature we should get a lowering of about  $4^{\circ}$  F. at midwinter, about the same as the amount I arrive at otherwise. This is not quite accurate, for we ought to take the 4th power from zero, not from  $-239$ , and also we ought to take the percentage diminution, not of the solar heat, but of the total heat. Still the calculation may help in a rough way to show the reasonableness of the results obtained in the paper.

\* Of course in strict accuracy we should use in the argument not  $54^{\circ}$  but the somewhat lower latitude whose midwinter sun-heat temperature at present is the same as that of  $50^{\circ}$  in the period of great eccentricity.

LXIV. *Description of a very Sensitive Form of Thomson Galvanometer, and some Methods of Galvanometer Construction.* By F. L. O. WADSWORTH\*.

[Plate XIV.]

A considerable interest has of late been manifested, particularly in Germany, in the construction of very sensitive galvanometers, a brief description of one, which has recently been constructed for the bolometric work of the Observatory, may not be out of place in connexion with my last article (p. 482). This galvanometer in question is of the Thomson type of construction with four coils wound under my instructions by Messrs. Elliot, Bros.

Fig. 1, Plate XIV., is a section through one of the coils showing the contour of the individual sections, of which there are five, of about 4 ohms each, in each coil. The size of wire, number of turns, and resistance in each section of one of the coils, which is typical of all of them, is given in the following table.

TABLE I.—*Coil marked A.*

Section.	Size wire.	No. of turns.	Resistance (at 20° C.).
No. I. (inner) .....	0.0065" (37 B.W.G.).	255	4.48 true ohms.
No. II. ....	0.012" (30 " )	410	4.21 " "
No. III. ....	0.021" (25 " )	640	4.13 " "
No. IV. ....	0.025" (23 " )	551	4.25 " "
No. V. (outer). ....	0.030" (22 " )	540	4.28 " "

Total number of turns . . . 2396.

Total resistance . . . 21.35 ohms.

The radius of the inner coil is 2 millim., and that of the outer coil 50 millim., and the depth of the coil was about 40 millim. As will be seen from the above table, the diameter of the wire increases somewhat less rapidly than the mean radius of the section, as required by Maxwell's theory, the thickness of the insulating covering, while not constant, being proportionally thicker for the finer than for the larger sizes†. The total number of turns in the four coils is 9593, and the total resistance (in series) 86 ohms at 20° C.

\* Communicated by the Author.

† Maxwell, Elec. and Magnetism, vol. ii. p. 363.

Each coil was cemented by means of melted shellac into an open brass case, which left the windings on the face of the coil exposed, and enabled them to be brought as close to the needle system as possible. These brass cases screwed into L-shaped supports, which rested on three adjustable screws—*a*, *b*, *c*, Plate XIV. (placed at three corners of the foot-plate of the L), the points of which slide in V-grooves planed in the metal plate which forms the base of the galvanometer-case. They are clamped in any desired position by means of a screw, *d*, working in a slot in the plate, as shown. This means of support allows the coils to be accurately centred with respect to each other, and, in conjunction with the levelling-screws on the case, to the needle system, independently of the adjustments of the latter. It also enables the coils to be readily removed whenever it is necessary to get at the needle, and the distance between the coils to be varied to increase or decrease the delicacy, without altering the astaticism of the system by means of a directing magnet.

The needle system itself is shown in fig. 4 (Pl. XIV.). The central staff is about 150 millim. long, drawn from glass tubing, and weighs about 5 mgs. On account of the length and thinness of the staff, special means of drawing it were necessary in order to get a perfectly straight piece.

A good method is to clamp a selected piece of tubing, about 5–10 millim. in diameter, in a retort-stand so it hangs vertical, and attach to the lower end a 4–5 lb. weight, which rests on some simple form of trap 4 or 5 feet above a box filled loosely with waste or shavings. The tube is heated uniformly by two good Bunsen burners until it begins to soften, then the burners are removed, the trap is immediately sprung, and the weight falls into the box placed to receive it, drawing out a thin tube of glass, the diameter of which will depend on the length of tube which has been softened. From a few fibres thus drawn a piece can be selected which will be satisfactory as regards straightness and lightness.

The two members of the system are built up each of ten small magnets, five on each side of the staff, the central one about 3 millim. long, and the upper and lower ones each a little less than 2 millim. They are made from the smallest size sewing-needles broken to the required length, but otherwise untreated\*. They were attached to the staff by first

\* This material is unsuited for the purpose, being too soft a grade of steel for retaining a high permanent magnetization. Some bars of special magnet steel were ordered, but have not yet been received, and pending their arrival the above material was used as the best available for the purpose. With steel of proper size, quality, and hardness, the magnetic moment could, I am certain, have been more than doubled, without any increase in weight.

cementing each set of five, in proper position, to a piece of thin tissue-paper, placing two sets face downward in the proper position, and at the proper distance apart, on a glass "flat," laying the glass staff on top of them, and cementing it to each by means of a very small drop of thick shellac. When dry enough to handle, the other two sets were attached to the other side of the staff, opposite the first two, in a similar manner. The mirror was then attached midway between the two members by means of a minute fragment of soft wax ("universal"), which touched the upper edge only of the mirror; a method more satisfactory than any other I have tried for mounting small thin mirrors without distortion.

This mirror was  $2\frac{1}{2}$  millim. in diameter and 1 millim. radius of curvature. It had an accurately worked surface (by Brashear) (rendered necessary by the fact that it is used for a photographic record), and had to be therefore quite thick and heavy for its size. The weight of the mirror was about 12 mgs., and the weight of the whole system about 40 mgs. It was magnetized and astaticized after being completed by the method described in my last article. The system was suspended by means of a fine quartz fibre, about 40 centim. long, whose tension was negligible. The method of supporting the fibre is in some respects novel, and has proved very successful in eliminating vibration, which, on account of the lightness of the system, at first proved very troublesome. The glass tube, *f*, of about 1 centim. bore, which carries at its upper end the adjustable head, *h*, to which the fibre is directly attached, is not directly connected with the galvanometer-case, but is supported by two thick rings of soft rubber, *m*, *n*, very slightly compressed between the glass tube and an outer heavy brass tube which is screwed to the top of the galvanometer-case. There is consequently no metallic or solid connexion between the fibre-support and the rest of the instrument, and the vibration which is communicated to the latter from the pier is absorbed by the rubber before it reaches the needle. It is also possible with this arrangement to attach the directing magnet to the outer brass tube without prejudicing the steadiness of the image during adjustment.

The damping of the needle is effected partly by a piece of dragonfly's wing attached to the back of the mirror and partly by four copper rods, which slide into the cores of the coils.

The coils on each side are connected in series, and the terminals brought up and connected to two copper binding-posts on the top of the case. The two sides could therefore

be connected either in series (resistance 86 ohms) or in parallel (resistance  $21\frac{1}{2}$  ohms); or by changing two connexions inside the case, all four coils could be put in parallel. Total (5 ohms) as desired.

The case was unusually large and heavy, with brass frame and glass sides, with all joints as air-tight as it was possible to make them. It had the usual doors and levelling-screws.

The constant of the galvanometer with the magnet system, already described\*, was for all coils in series,  $C = 4 \times 10^{-11}$ , where  $C$ , as before, is the current in amperes required to produce a deflexion of 1 millim. at a distance of 1 metre for a time of single swing of 10 sec. This is about the degree of delicacy recently attained by Snow †, the constant of whose instrument reduced to the units above used was  $C = 4.5 \times 10^{-11}$  for a somewhat higher resistance (140 ohms).

More recently, Paschen ‡ has attained a degree of delicacy considerably exceeding this by the use of an excessively light magnetic system, which did not appear to be stable enough to be actually used with a 10 sec. period in measurement.

The question of the influence of the mass of the system on the delicacy is one of importance. It was first pointed out by Boys, and later by Paschen, that if a fixed time of vibration be considered, the sensitiveness of the galvanometer (other things being equal) will increase as the mass of the system decreases. This has been experimentally verified by Du Bois and Rubens, who, by the use of light magnetic systems, have recently produced commercial galvanometers having a sensitiveness nearly equal to that of Snow's instrument §.

But the assumption of a fixed time of vibration is unfair to the heavier systems, for it conditions them to a degree of more and more imperfect astaticism as the weight increases. If, instead of the condition of a fixed time of vibration, we impose that of a fixed degree of astaticism, viz., if we make the residual magnetic moment of the systems as a whole constant, then the sensitiveness of the galvanometer will *increase* with the mass of the magnetic system, supposing always that the coils of the instrument are suitably proportioned to the needle. A better understanding of these points is afforded by their analytical expression. We will suppose

\* As has already been stated in a previous footnote, this system could be very sensibly improved, but as the sensitiveness of the galvanometer even with the present system is greater than necessary, and as my time has been fully occupied with other work, this has not yet been done.

† Wied. *Ann.* vol. xlvii. p. 218 (1892).

‡ *Ibid.* vol. xlviii. p. 284 (1893).

§ Wied. *Ann.* vol. xlviii. p. 236 (1893).



for convenience that each member of the system is equivalent to a circular disk whose diameter,  $2r$ , is equal to the length of the longest magnet of the system, and whose thickness,  $w$ , is such that the mass of the disk is equal to the sum of the masses of the individual magnets \*. Then the mass of the disk will be  $A r^2 w$  and its moment of inertia  $B r^4 w$ . The mass and moment of inertia of the mirror will be  $A' r_0^2 w_0$  and  $B' r_0^4 w_0$  respectively.

Then, if  $t$  denote the time of single swing,  $M$  the residual magnetic moment of the system, and  $H$  the strength of the field in which the system swings :—

$$t = \pi \sqrt{\frac{I}{MH}} = \pi \sqrt{\frac{B w r^4 + B' w_0 r_0^4}{MH}}.$$

The moment of the force required to produce unit deflexion,  $\theta$ , of the system is  $F C m$ ; where  $C$  is the current flowing in the coils,  $m$  the individual magnetic moment of one member of the system, and  $F$  a constant involving the constant of the coils, the intensity of magnetization, &c.; and it is also equal to  $M H \theta$ . Therefore

$$MH = F/\theta \ C m = F' C w r^2,$$

since the magnetic moment is, for the same intensity of magnetization in different disks, proportional to the mass of the disk, that is to  $w r^2$ .

Therefore, finally,

$$t = \pi \sqrt{B'' \frac{r^2}{C} + \frac{B'''}{C}}.$$

Hence, if  $t$  is constant,  $C$  varies as  $r^2$  plus a constant; that is, the sensitiveness increases somewhat less rapidly than the mass of the system diminishes. But if no limit is imposed on the time of vibration, but only on the final degree of astaticism, then  $MH = \text{const.}$ , hence  $Cm = \text{const.}$ , or the sensitiveness varies directly as the magnetic mass. It is true that the conditions of use impose the former rather than the latter limit, but for an average time of single swing of 10 sec., which is not inconveniently long, I believe that a system weighing from 40 to 60 mgs. will be found best, for if very great sensitiveness is required, we can use a time of swing of from three to four times this without as great inconvenience as would result from the use of a system only

\* It is not of importance here to consider the most effective form or arrangement of individual magnets, as we are only considering relations between systems of the same form, but of varying dimensions.

one tenth as heavy with a 10 sec. period. With very light systems the mirror is unduly heavy in proportion to the weight of the magnet systems, and the difficulty of handling, and especially of astaticizing, is much increased. Their principal disadvantage, however, is their extreme sensitiveness to vibration. A system weighing 25 mgs. was first used in the galvanometer described above, but it was found absolutely unfit for photographic work because of the unsteadiness of the image.

Indeed, even with the heavier system, the complete elimination of the effects of vibration proved a troublesome problem, for the Observatory is in close proximity to several traffic-laden streets, and the work had necessarily, because of its nature, to be carried on during the busiest part of the day. Very good results were finally obtained by use of the insulated fibre support, already described, in conjunction with the use of rubber blocks between the slab of stone on which the galvanometer was mounted and the pier which supported the whole. Under very favourable circumstances a somewhat lighter system than the one here recommended could no doubt be used; but in the great majority of cases I believe that the weight should not be less than 30 to 40 mgs., and may with advantage be considerably more.

Astro-Physical Observatory,  
Washington, June 1893.

## LXV. *Telephonic Measurement of Electromotive Force.*

By CARL BARUS\*.

1. **PURPOSE.**—Notwithstanding the varied use which has been made of the telephone in electrical measurement, I am only aware of isolated efforts† to replace the galvanometer by the telephone in the zero methods for electromotive force. Yet, according to the earlier observers, the telephone ought to be more than sufficient for the purpose (§ 2). The problem suggested itself to me in connexion with thermoelectric pyrometry, where an avoidance of the galvanometer would often facilitate the work. Recently I thought of it again in relation to certain meteorological experiments, in which temperatures are made to vary in rapid rhythm by condensation, and the object is to find the thermal amplitude and the character of the oscillation. It thus becomes necessary to vary the electric contacts in like rhythm and to find

\* Communicated by the Author.

† Ledebøer, *Beiblätter*, ix. p. 357 (1885).

the temperatures for all differences of phase between the two pulsations thermoelectrically by a zero method. Here, therefore, the instantaneous telephonic registry would have advantages over the galvanometer, aiding the ear something after the manner in which the stroboscope assists the eye.

Contrary to my expectations, however, great difficulty was encountered in endeavouring to make the telephone sensitive enough; and the work resulted in showing that the range of increments of the magnetic field on both sides of zero, within which the telephone does not respond, is out of proportion with the sensitiveness of the instrument. It is the aim of this paper to find the extent and character of this silent interval, in its relations to the method in question.

2. *Literature*.—The earlier history of the subject is summarized in Wiedemann's *Elektricität*\*, vol. iv. p. 285 (1885), and need not be repeated here. Recently a series of remarkable researches have appeared, due respectively to Prof. C. R. Cross and his pupils† and to Lord Rayleigh‡. In the former the excursions of the telephone diaphragm are mapped out in their dependence both on the intensity of the magnetic field and of the actuating line-current. The occurrence of a marked maximum of sensitiveness for a certain intermediate value of the magnetic field is clearly shown among other data of value. The line-currents, however, are in magnitude above those of the present paper.

Lord Rayleigh's recent research covers much of the ground of my own work §, and it leads to the same order of results, in so far as data somewhat different in character (§ 5) are comparable. My chief reason for publishing the present paper is, therefore, the special point of view mentioned at the end of § 1.

3. *Apparatus*.—A diagram of the connexions, with special reference to the construction of the key, is given in fig. 1. The two circuits in action are  $aREBCsra$  and  $aTeACsra$ , where  $e$  is the weaker cell to be compared with the constant cell  $E$ .  $R$  and  $r$  are rheostats,  $T$  the telephone,  $s$  a coiled wire or spring introduced to allow easy motion of the metallic plate  $C$  of the key.

\* The works of Warren De La Rue, Brough, Pellatt, Ferraris, and others being referred to. The theoretical researches of Tait and of Preece are mentioned by Lord Rayleigh.

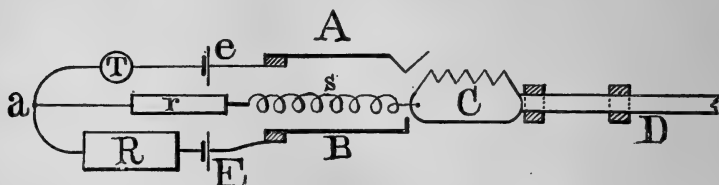
† Cross and Hayes, *Proc. Amer. Acad.* xxv. p. 233 (1890); Cross and Phillips, *ibid.* Jan. 1893; Cross and Mansfield, *ibid.* May 1892.

‡ *Phil. Mag.* xxxviii. p. 285 (1894).

§ My note in the *American Journal*, October 1894, p. 346, was in press before the advance account of Lord Rayleigh's work (in 'Nature') reached me.

Contact is made by aid of two flat springs A and B, on moving the plate C between them by aid of the handle or

Fig. 1.



guide D. C being wider on one side than on the other, the circuit  $aEBCsra$  is first closed; after this the circuit  $aTeACsra$  is closed; and since the shorter side of the key C is provided with a serrated edge, sounds will in general be heard in the telephone, T, on pushing the plate C quite past the springs A and B either from left to right or in the opposite direction. If the resistances  $r$  and  $R$  are large as compared with the rest of the circuits, the telephone will cease to respond when  $e/E = r/(R+r)$ , which is the adjustment sought.

As the telephone is less sensitive than a good galvanometer, every precaution must be taken to use it to the best advantage. It is necessary to pass a bifurcated tube from the sound-chamber to the ears, and the key mechanism A C B D should be placed at a distance and operated either by a long stick or cord, or preferably by the pneumatic device so much used in photography. The plate C is best made of copper (like the circuits), and need not be more than 2 centim. long. The teeth should be coarse, say about 0.5 centim. from point to point, and the V-shaped very thin flat spring at the end of A should only just touch the ends of the teeth when C moves across the spring. In this way a minimum of noise is made in the air, the successive taps are sharply individualized, and the circuit is kept closed only during very short intervals of time (avoidance of polarization). Blunt teeth were tried without advantage, and merely to warrant the use of equation (1), § 4.

The construction of the key\* is a matter of great importance, for the sensitiveness of the method depends on it. Indeed I have found different telephones behave quite differently relatively to each other when the method of making the contact was varied; a result agreeing with the experience of

\* Regular rhythmic interruption like that produced by a tuning-fork would possibly increase the sensitiveness; but the use of such cumbersome apparatus is of course out of the question.

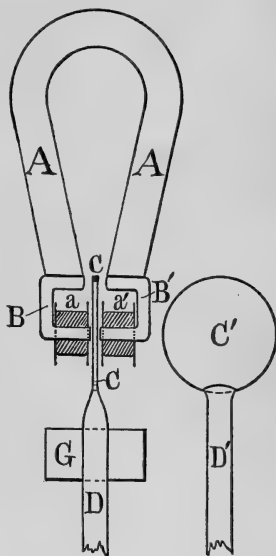
Lord Rayleigh (*l. c.* pp. 294-5). With the key given the sound of each tap is wheezing, so that the overtones come into play. The enormous advantages of notes of high pitch over those of low pitch for purposes like the present has been shown both by Ferraris and, more remarkably, by Lord Rayleigh.

In addition to the Bell telephone I made use of the duplex form\* shown in fig. 2. Here A A is an ordinary horse-shoe magnet provided with two similar U-shaped armatures of soft iron B, B'. These carry the telephone coils *a*, *a'*, the terminals of which lead to four clamp-screws (not shown), so that a current may be passed through the coils either in series, or in parallel, or differentially. Between the coils the discoid hollow sound-chamber C C, the walls of which are thin (·016 centim.) circular plates of iron, is secured by clamping the wide tube D, which conveys the sound to the ears, to the flat-topped upright G. A side view of the sound-chamber with its efflux-tube is shown detached at C' D'. The whole is soldered firmly together at the edges, these being spaced by a ring of copper wire.

The armatures B, B' are adjustable, and may be moved as close to the disk C C as desirable (set screws not shown). The plates of C vibrate symmetrically, changing the form from biconvex to biconcave, and I obtained the best results with chambers 4 centim. in diameter and about 0·2 centim. deep. When the chamber is more shallow the magnetic field is strengthened, but the sound probably encounters too much resistance in passing out into the air.

In view of the large resistances R and *r* (fig. 1), the coils of the telephone were made of 0·01 centim. wire, wound so that as many as 3000 turns could be brought to bear on each armature, with resistances as high as 300 ohms (see table below). The advantage of the double form is to be found in the ease with which the coils may be replaced by others, in

Fig. 2.



\* Duplex telephones were first introduced by Elisha Gray.

the economic disposition of the wire relative to resistance, and in the strong field of induction normally through the diaphragms even when the magnet A is not remarkably strong. The chief condition of sensitiveness is close approach of the coil ends of the armature to the two walls of the sound-chamber, respectively. Hence this adjustment must be made with care and the diaphragms must not buckle. I usually placed armature and diaphragm in actual contact on one side and all but in contact on the other, and then tapped the sound-chamber into position.

Among other devices for increasing the sensitiveness of the telephone I may mention the endeavour to follow the excursions of the Bell diaphragm by a microphonic contact\*. My best results were obtained by soldering a platinum stylus axially to the centre of the diaphragm. The end of the stylus just touched a little pellicle of carbon suspended by a delicate spring, the arrangement being in circuit with four Leclanché cells and a second telephone. With this relay apparatus sounds above a certain intensity were greatly increased, while sounds of lower intensity were either left unchanged or even extinguished, and the degree of sensitiveness varied too rapidly for convenience or certainty of measurement. Similarly ineffectual efforts were made in adapting transformers and condensers for the purpose.

4. *Results*.—The current  $i'$  passing through the telephone during the time of contact, considered apart from self-induction†, may be expressed under the form

$$i' = \frac{e}{R} \frac{\frac{E}{r'} - \frac{r}{R+r}}{\frac{r}{R} + \frac{r}{R+r}}; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $r'$  is the resistance of the shunt containing the telephone and the electromotive force  $e$ ,  $R$  the resistance of the shunt containing the electromotive force  $E$ , and  $r$  the resistance of the remaining branch circuit. If, therefore, by any independent means the ratio  $e/E$  has been found, equation (1) is available for computing  $i'$ . The necessary data are obtainable without auxiliary measurements of  $e/E$  by taking advantage of *both margins* of the interval of silence already alluded to in § 1, in the way presently to be shown.

In the following table I shall therefore, in addition to the

\* Somewhat similar experiments were made by Messrs. Thomson and Houston; also by Hughes and others.

† Tested by the blunt-toothed key (§ 3) and found admissible.

quantities just specified, give under  $\delta i'$  the smallest increment of  $i'$  in microamperes just audible on either side of the interval of silence, and under  $\Delta i'$  the extent of this interval. In other words, if  $i_1', i_2', -i_3', -i_4'$  are two pairs of currents just distinguishable in loudness, one pair at each margin of the interval of silence, then

$$\delta i' = \frac{1}{2}((i_1' - i_2') + (i_4' - i_3')), \quad \Delta i' = i_2' + i_3'.$$

Sound therefore just ceases (marked ?) for currents  $i_2'$  and  $i_3'$  on either side of zero, and is just audible for currents  $i_1'$  and  $i_4'$  on either side of zero. Inasmuch as the values  $i_1' i_2'$  and  $i_3' i_4'$  may be considered symmetrical with respect to  $i' = 0$ , the value of  $e/E$  can be found by taking the mean of the measurements for  $i_2'$  and  $i_3'$  with an accuracy of one half the sensitiveness of the telephone at the margins of the silent field. It is for this reason that the inertness of the telephone is no serious drawback, apart from the time lost in making an extra observation. Thus, for instance, the following four values of  $e/E$  correspond to  $i_1', i_2', i_3', i_4'$ ,

$$e/E = 4990, \quad 4996, \quad 5028, \quad 5034,$$

whence, by taking symmetrical terms,  $e/E = 5012$ .

TABLE showing Sensitiveness of Telephones.

Signal.	$i'$ .	$\delta i'$ . $\Delta i'$ . $\delta i' / \Delta i'$ .	E. $e/E$ . R. $r$ .	Remarks.
Noise.	-2.9	.9	2	Double telephone* (fig. 2). Fine-toothed key.
?	-3.8	7.6	.503	
?	+3.8	9	4950	
Noise.	+2.8	...	5000	
Noise.	-2.4	.4	2	Do.*
?	-1.9	3.9	.490	
?	+2.0	9	10400	
Noise.	+2.4	...	10000	
Noise.	-2.2	.2	2	Do.*
?	-2.0	3.9	.492	
?	+1.9	15	20700	
Noise.	+2.2	...	20000	
Noise.	-1.5	.2	2	Do.* With new sound-chamber.
?	-1.3	2.5	.501	
?	+1.2	10	20500	
Noise.	+1.5	...	20000	

\* Coils with 1200 turns each, 1.25 centim. long, .8 centim. internal diameter, 1.4 centim. external diameter.

Table (*continued*).

Signal.	$i'$ .	$\delta i'$ . $\Delta i'$ . $\delta i' / \Delta i'$ .	E. $e/E$ . R. $r$ .	Remarks.
Noise. ? ? Noise.	-1.3 -1.1 +1.1 +1.3	.2 2.2 9 ...	2 .500 20050 20000	Double telephone*.
Noise. ? ? Noise.	- .9 - .6 + .6 + .9	.2 1.2 5 ...	2 .500 20050 20000	Do.* Coils nearer diaphragm.
Noise. ? ? Noise.	-.43 -.31 +.31 +.43	.12 .62 5.2 ...	2 .501 19970 20000	Do.* New coarse- toothed key.
Noise. ? ? Noise.	- .9 - .6 + .6 + .9	.2 1.2 5 ...	2 .500 20050 20000	Do.* Coils in parallel.
Noise. ? ? Noise.	-4.4 -4.0 +3.7 +4.2	.5 7.7 16 ...	2 .486 21300 20000	Bell telephone, low resistance, plate .02 centim. thick.
Noise. ? ? Noise.	-4.2 -3.7 +3.5 +4.0	.5 7.2 15 ...	2 .489 21000 20000	Bell telephone†, high resistance, plate .02 centim.
Noise. ? ? Noise.	-2.0 -1.5 +1.4 +1.9	.5 2.9 6 ...	2 .494 20500 20000	Same with tin plate .016 centim.
Noise. ? ? Noise.	-3.1 -2.6 +2.5 +3.0	.5 5.1 11 ...	2 .496 20000	Same with plate reversed.
Noise. ? ? Noise.	-2.1 -1.6 +1.6 +2.0	.5 3.2 7 ...	2 20350 20000	Same with iron plate .018 centim.
Noise. ? ? Noise.	-1.0 - .8 + .7 +1.0	.2 1.5 6 ...	2 .501 20000 20000	Same with tin plate .030 centim., and tin plate .016 centim.

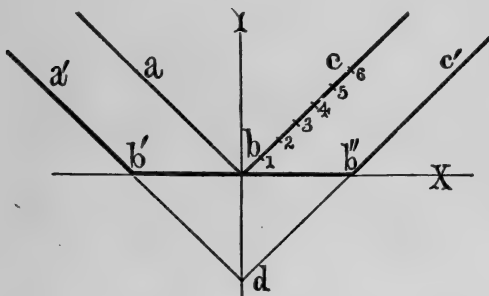
\* Coils with 3000 and 3600 turns respectively, 1.25 centim. long, .8 centim. internal diameter, 2.5 centim. (about) external diameter.

† Coil with 2400 turns, 1.25 centim. long, .8 centim. internal diameter, 2 centim. external diameter.



5. *Inferences.*—The chief result in these series of data (and more might be added) is the occurrence of the silent field, whose extent,  $\Delta i'$ , is fully 5 to even 15 times the interval,  $\delta i'$ , within which change of sound-intensity is appreciable when the limits of the field in question are exceeded. Thus the phenomenon remained unchanged in character when different resistances  $r$  and  $R$  were introduced, when the coils of the double telephone were replaced by others, or when the sensitiveness was changed in marked degree. This was also the case with the Bell telephone for different coils, diaphragms, keys, &c. With allowances for the difficulty of estimating faint sounds, the extent  $\Delta i'$  of the silent interval decreases as the sensitiveness of the telephone increases, a result to be anticipated; but the case is always one involving a true discontinuity. Thus if the intensity of the current in the helix be laid off as abscissa and the sound-intensity as ordinate, one would expect to find a curve like  $abc$  (fig. 3), where the

Fig. 3.



equidistant points 1, 2, 3, ... represent appreciable differences of loudness, and the symmetrical branches converge at the origin of coordinates. The curve actually found has the form  $a'b'b''c''$ . Sound ceases before the otherwise audible current increments are quite expended, so that the part  $b'db''$  of the converging curve is truncated.

The sensitiveness of the telephones was found to be largely dependent on the construction of the contact-key, a statement already made in § 3. However, under my best conditions shades of intensity of less than  $10^{-7}$  ampere were acoustically indistinguishable, not to mention the much larger interval of silence which intervened. The results thus obtained are, therefore, less encouraging than the data given in experiments of De La Rue, Brough, Pellat, Ferraris, and others\*,

\* I have stated that my experiments were made at the incentive of the earlier researches.

in all of which a current at least as small as  $10^{-8}$  amperes is pronounced audible, would indicate, not to mention the more striking results of Tait and Preece. They agree in order with the data of Lord Rayleigh for frequencies between 300 and 500. Perhaps, however, it would be more fitting to regard the extent of the silent interval as the sensitiveness of the telephone, in which case my results are of the order of those found by Lord Rayleigh for the 4-foot octave.

Throughout my work, it will be remembered, the telephone was excited by isolated taps, and pains were taken to assist the ears by aid of sounding-tubes. One therefore expects a difference of behaviour in the two cases.

In relation to the measurement of electromotive force, therefore, the telephone does not quite come up to the requirements. By using the shades of audibility at the margins of the silent interval for the determination, it is possible to define electromotive forces of the order of one volt with an accuracy of one in one thousand. For thermoelectric forces like those occurring in pyrometry, the telephonic method is available only in rough work. Thus a single iridio-platinum couple (20 per cent. iridium in the alloy), with its hot junction kept at low red heat, showed the following values of apparent electromotive force,  $e$ , at the margins of the silent field:—

Noise.	$e=9800$ microvolt.	} Mean	Temperature = $837^{\circ}$ C.		} Mean
?	9752		9480	$834^{\circ}$	
?	9212		micro-	$795^{\circ}$	
Noise.	9170		volt.	$792^{\circ}$	
					$815^{\circ}$ C.

The temperatures corresponding to the two apparent values of thermoelectromotive force on each side of the silent field have been added. Hence the interval of silence corresponds to about  $40^{\circ}$  Centigrade; but the sensitiveness at the margins of the interval is such that the mean temperature deduced is in error only  $2^{\circ}$  or  $3^{\circ}$ . However, close measurement like this can be made only under conditions of exceptional silence in the surroundings. In a noisy room increments of less than  $10^{\circ}$  at  $1000^{\circ}$  will escape detection, though the results will be more favourable in proportion as temperature increases.

In endeavouring to account for the occurrence of the silent interval, one may note first that the thickness of the diaphragm has little influence within the limits of  $\cdot 015$  centim. to  $\cdot 030$  centim. employed. The range of silence does decrease, however, when the telephone is made more sensitive either by modifications of the key or, again, by moving the armatures and coils closer to the diaphragm when other things are left unchanged. In such cases the forces actuating the plate are

increased. To invoke the inertia of the plate seems inadmissible, seeing that telephones with diaphragms \* fifteen (15) centimetres thick have been made to respond (Bréguet).

I have therefore hazarded a straightforward supposition †, that the interval of silence is to be referred to a molecular inertness of the plate of the telephone very similar in its nature to quiescent friction. The diaphragm at rest seems initially to resist further deformation, and this resistance must first be overcome before the telephone will respond with nicety to fine gradations of the actuating stress. In other words, as soon as the internal friction encountered in moving the diaphragm has passed from the quiescent to the kinetic stage, the instrument is ten or more times more sensitive than it was before the critical stress value had been exceeded.

Washington, D.C., U.S.A.

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LXVI. *Note on the Measurement of the Specific Inductive Capacities of Water, Alcohol, &c.* By REGINALD A. FESSENDEN, *Professor of Electrical Engineering, Western University of Pennsylvania*‡.

IT appears to have been hitherto accepted that the high values for the specific inductive capacities for water, alcohol, and some other similar fluids which have been obtained by various experimenters are correct. If this were so, Maxwell's rule for the relation between specific inductive capacity and the index of refraction would not hold in these cases for wave-lengths of visible light, and the phenomena of dispersion &c. have been called in to explain this anomaly. It may be well to point out that these high values are not correct, but that the true values are in every one of these substances very nearly equal to that called for by the theory.

This fact was first noticed by the writer in 1891. A sensitive electrometer had been constructed, with two fixed and one movable cylinder, mounted on jewels, and provided with a commutator, so as to act as an electrostatic wattmeter. With a pressure of 1000 volts on the fixed and 50 volts on the movable part, it made 300 revolutions per minute. At

\* Cf. Du Moncel's 'Telephone,' American edition, p. 115, containing an account of experiments due to Bréguet and to Bell.

† References to hysteresis, to inconstancy of the batteries, &c. seem inadmissible.

‡ Communicated by the Author.

low speeds, however, the friction threw the readings out a good deal. It then occurred to the writer to utilize the suggestion made by Messrs. Swinburne and Kelly for electrostatic voltmeters, *i. e.* to immerse the instrument in oil. This was done with good results. It was reasoned, then, that since pure water insulates as well as indiarubber, and has, according to the experimenters referred to above, a specific inductive capacity of over 70, or 35 times that of oil, all difficulties would be removed by its use. Water distilled *in vacuo* to remove foreign gases was then tried, but gave no better results than oil. The commutator was then taken off and the movable cylinder suspended by a bifilar suspension, with the result that in the case of oil and the alcohols the specific inductive capacity came out very nearly equal to the square of the refractive index, thus showing plainly that all the high determinations hitherto given were erroneous.

The reason of these errors was not far to seek. It lay in the fact, pointed out by Maxwell and others, that electrolysis gives a capacity effect. A number of determinations made by students in my laboratory show that, for 133 periods per second, and a current-density of .01 ampere per square centim., each square centim. of electrode-surface has an apparent capacity of 400 microfarads when the electrolyte is caustic soda and the plates nickel. It is for this reason that Kohlrausch's method almost always gives erroneous results, as what is measured is not the resistance of the electrolyte, but its impedance.

Since Messrs. Cohn and Arons, for example, used an induction-coil to charge the plates of the electrometer immersed in water, it follows that the voltage on the water-immersed quadrants might easily have been 100 times that on the other quadrant, and that the method is inapplicable. All capacity measurements made by discharge are also incorrect; and the only correct method consists in purifying the fluid till it no longer conducts appreciably, and then measuring the attractive force between the plates when these are charged from a continuous current source of high voltage. Either a torsion or chemical balance may be used. A certain amount of leakage will always take place, but this must be provided for by using a powerful source of current.

It might also be mentioned that all the determinations of specific capacity of substances such as sulphur &c. are incorrect. For the reasons of this, those writers who have treated of the capacity of laminated dielectrics may be consulted.

LXVII. *The Influence of the Relative Volumes of Liquid and Vapour on the Vapour-Pressure of a Liquid at Constant Temperature.* By SYDNEY YOUNG, D.Sc., F.R.S., University College, Bristol\*.

THE question whether the vapour-pressure of a liquid at a given temperature depends on the relative volumes of liquid and vapour has been frequently discussed, and has been the subject of many experimental investigations. Within recent years extended researches on the relations between the temperatures, pressures, and volumes of several liquids have been carried out by Prof. Battelli, and he arrives at the conclusion that when, in a tube containing a perfectly pure liquid and its vapour, the volume is diminished and the vapour caused to condense, the vapour-pressure rises : in other words, that the smaller the relative volume of vapour the higher is the vapour-pressure.

These results are entirely opposed to those obtained by Dr. Ramsay and myself and, while referring to this question in a letter to the 'Philosophical Magazine' last February, we ventured to characterize the conclusions of Prof. Battelli as incorrect, and to suggest that the error was due to the presence of small quantities of air or other impurity in the liquid examined and to the employment of insufficiently purified substances for heating-purposes.

In a letter published in the August number of the 'Philosophical Magazine' Prof. Battelli adheres to the conclusion previously stated, and does not admit the existence of either of the sources of error suggested. "I would rather observe," he writes, "that, in order to observe such a phenomenon, an apparatus is necessary which enables us—as in my case—slowly to compress the vapour, and to maintain it for a time under constant pressure."

There can be no doubt, I think, that such an apparatus is required in order to decide *the question whether the phenomenon exists*, but it seems hardly necessary to point out that the conditions described are fulfilled in the apparatus employed by Dr. Ramsay and myself.

During the present year I have been engaged in an investigation of the thermal properties of isopentane—a liquid, boiling at 28°, which can, by suitable treatment, be obtained in a pure state †.

\* Communicated by the Physical Society: read November 9, 1894.

† Full details of the method of purification adopted will be described later when the research is completed.

A great number of determinations of the vapour-pressure of the liquid were made at various temperatures, and in many cases the volumes of liquid and vapour were read. The results obtained prove conclusively that the vapour-pressures of isopentane are independent of the relative volumes of liquid and vapour; and it may be of interest to give all the observed vapour-pressures at two temperatures, with the corresponding volumes of vapour and liquid.

The same apparatus was employed as in my previous work on benzene and its derivatives, the esters, &c.: it is similar in principle though it differs somewhat in detail from that made use of by Ramsay and myself (*Phil. Trans.* 1887 A, p. 59).

The tube containing the isopentane was heated by the vapour from pure liquids (*Trans. Chem. Soc.* 1885, p. 640; 1889, p. 483) boiling under reduced pressure.

The pressures are corrected for (1) the difference in height of the columns of mercury in the tube containing the isopentane and in the air-gauge; (2) the expansion of the heated column of mercury; (3) the pressure of the column of isopentane; (4) the deviation of air (in the air-gauge) from Boyle's law, as determined by Amagat.

Several series of determinations were made with different quantities of liquid in the tube. As a rule four readings of pressure were taken in each series at each temperature.

It will be seen that although the relative volumes of vapour and liquid vary within very wide limits, there is no such corresponding variation in the vapour-pressures, the greatest difference from the mean value at  $140^{\circ}$  being slightly less than 0.1 per cent., and at  $90^{\circ}$  slightly greater—in no case outside the limit of experimental error.

It has happened occasionally in the course of this or previous investigations that a trace of air has entered the tube or has been left in the liquid, and in a very few cases (ethyl formate, propyl formate) a small quantity of permanent gas has been formed by partial decomposition of the liquid by prolonged heating at high temperatures. The presence of permanent gas (or of very volatile impurity) is clearly indicated by the increase of pressure required for the complete condensation of the vapour, and the following points have been noticed in such cases:—(1) The pressure does rise as the volume of vapour diminishes; (2) the readings taken with diminishing volumes are higher than with increasing volumes. This may be readily explained; for when the whole of the substance is in the state of vapour the air is diffused uniformly through it, and when condensation is brought about

Temperature = 90°.					
Series.	Volume of Vapour in c.c.'s.	Volume of Liquid in c.c.'s.	Ratio { $\frac{\text{Volume of Vapour.}}{\text{Volume of Liquid.}}$	Vapour-Pressure.	Difference from Mean.
II. ....	0.016	0.52	0.03	4280	-1
III. ....	0.025	0.20	0.12	4281	0
II. ....	0.105	0.52	0.20	4286	+5
I. ....	0.07	0.23	0.30	4281	0
,, ....	0.17	0.23	0.74	4280	-1
III. ....	0.17	0.19	0.89	4279	-2
I. ....	0.28	0.23	1.2	4281	0
III. ....	0.30	0.19	1.6	4277	-4
I. ....	0.38	0.23	1.7	4282	+1
III. ....	0.42	0.19	2.2	4281	0
Temperature = 140°.					
II. ....	0.012	0.54	0.02	11636	-2
,, ....	0.06	0.54	0.11	11634	-4
III. ....	0.06	0.20	0.30	11643	+5
I. ....	0.08	0.24	0.33	11637	-1
IV. ....	0.06	0.07	0.86	11638	0
I. ....	0.20	0.23	0.87	11636	-2
III. ....	0.20	0.18	1.11	11643	+5
V. ....	0.07	0.06	1.2	11634	-4
I. ....	0.32	0.21	1.5	11641	+3
III. ....	0.34	0.17	2.0	11649	+11
I. ....	0.43	0.20	2.2	11642	+4
III. ....	0.48	0.16	3.0	11647	+9
IV. ....	0.23	0.05	4.6	11633	-5
V. ....	0.26	0.04	6.5	11635	-3
IV. ....	0.39	0.03	13.0	11632	-6
V. ....	0.45	0.02	22.5	11636	-2
IV. ....	0.56	0.02	28.0	11634	-4
V. ....	0.62	0.002	310.0	11632	-6

by compression the air remains to a large extent in the vapour above the liquid and dissolves but slowly in the liquid formed; consequently, as the volume of vapour diminishes the undissolved air becomes more and more compressed, and its pressure increases and becomes considerable when the vapour is nearly all condensed. Similarly, with an impurity more volatile than the pure substance, a partial "fractionation" of the liquid takes place, the less volatile pure substance condensing first, whilst the vapour becomes more and more contaminated with the more volatile impurity.

On the other hand, when the readings are taken with increasing volume, the air or volatile impurity is at first uniformly distributed through the liquid, and it escapes but slowly through the long column of liquid into the vapour above. Thus when a reading is taken with a relatively small volume of vapour, the air present has a much greater influence in the first case than the second, but when the volume of vapour is relatively large its influence is small in both cases. I have noticed repeatedly that the freer a liquid is from air or permanent gas, the more closely do the readings during compression and expansion agree.

The presence of a small quantity of impurity less volatile than the pure substance may escape detection so long as the volume of liquid, relatively to that of the vapour, is fairly large; but its influence becomes very marked when the quantity of liquid is relatively very small. Thus, on one occasion, the isopentane had come in contact for a moment with an indiarubber tube and had, no doubt, dissolved a minute quantity of it. It was noticed in this case that the mercury was slightly tarnished (owing in all probability to the sulphur in the indiarubber), but the vapour-pressures, when there was plenty of liquid present, agreed among themselves and with previous determinations. When, however, the volume was increased until nearly the whole of the liquid was evaporated, the observed vapour-pressures were far too low, and diminished rapidly as the volume was increased.

In this case and in those in which the presence of any permanent gas was detected, the experimental results were rejected and the tube was refilled.



LXVIII. *Proceedings of Learned Societies.*

## GEOLOGICAL SOCIETY.

[Continued from p. 504.]

June 6th, 1894.—Dr. Henry Woodward, F.R.S., President,  
in the Chair.

THE following communications were read:—

1. 'On the Banded Structure of some Tertiary Gabbros in the Isle of Skye.' By Sir Archibald Geikie, LL.D., D.Sc., F.R.S., F.G.S., and J. J. H. Teall, Esq., M.A., F.R.S., Sec.G.S.

After calling attention to the previous references to the pseudo-bedding and banding of the gabbro-masses of the Inner Hebrides, the authors describe the rocks which form the rugged ridge of Druim-an-Eidhne, near the head of Glen Sligachan. This ridge is made up of parallel beds, sheets, or sills disposed in a general N.N.W. direction with a prevalent easterly dip. Four distinct types of gabbro occur:—(1) dark, fine-grained, granulitic gabbros; (2) well-banded gabbros; (3) coarse-grained massive gabbros; and (4) pale veins of a highly felspathic gabbro. The relative ages of the banded and granulitic gabbros have not been definitely settled; but the coarse, massive gabbros are certainly intrusive in the banded series and the pale veins cut all the other varieties.

The paper deals mainly with the banded gabbros. They occur in successive sheets or sills which vary from a few feet to many yards in thickness, and consist of parallel layers of lighter and darker material which correspond in direction with the trend of the sheets, and are usually inclined to the east or south-east at angles ranging from  $20^{\circ}$  to  $30^{\circ}$ . In some cases the bands can be seen to have been puckered or folded.

The minerals entering into the composition of the banded, as also of the other varieties, are labradorite, pyroxene, olivine, and titaniferous magnetite. The banding is due to a variation in the relative proportions of the different constituents and especially in the amount of magnetite. Some narrow bands and lenticles are composed entirely of pyroxene and magnetite. The variations in chemical composition are illustrated by three analyses by Mr. Player. The microscopic characters of the rocks are described, and it is shown that the minerals of the banded gabbros have not been crushed or broken since they were formed.

The authors conclude that the banding is the result of the intrusion of a heterogeneous magma and that similar banding in certain portions of the Lewisian gneiss may have been produced in the same way.

2. 'On the Microscopical Structure of the Derbyshire Carboniferous Dolerites and Tuffs.' By H. H. Arnold-Bemrose, Esq., M.A., F.G.S.

The paper deals with the petrography of the Toadstones or igneous rocks of Derbyshire. Brief reference is made to the work of previous petrographers, the age of the rocks, and the question as to the number of beds. The outcrops mapped by the Geological Survey, and several additional ones, have been examined, and the results given in a table for the purpose of the paper and for future reference.

The Toadstone is divided into massive rocks or lavas, and fragmental rocks or tuffs. The former consist of olivine-dolerite, either with granular or with ophitic augite, and olivine-basalt. The rock is often very fresh, but in some places is altered to a diabase. The principal constituent minerals are described. A pseudomorph of olivine, optically like biotite and somewhat like Iddingsite but differing from it chemically, is fully described.

The latter portion of the paper deals with the tuffs, which are much more extensive than has been hitherto supposed. Specimens are described, taken from thirteen outcrops.

3. 'On the Origin of the Permian Breccias of the Midlands, and a Comparison of them with the Upper Carboniferous Glacial Deposits of India and Australia.' By R. D. Oldham, Esq., F.G.S.

The author first describes the Permian Breccias of the Midland Counties of England, which he had the opportunity of examining at Eastertide of the present year. He describes the characters of the Breccias, and concludes that they were formed subaërially as gravel-fans by rivers charged with a maximum load of sediment, and therefore incapable of performing any appreciable amount of erosion. An examination of many of the fragments at Abberley and some at Church Hill reveals the presence of scratches, which occur in such a manner that the author believes they existed on the fragments before they were transported, and discusses the evidence for their production by ice or soil-cap movement, deciding in favour of the former.

A short description of the Upper Carboniferous deposits of India follows, and it is pointed out that they differ markedly from the deposits of Britain. Amongst other things the separation of different pebbles by considerable interspace of matrix, and the bending of stratification-planes round a pebble as though the pebble had dropped from above, is noted, and it is maintained that floating ice alone will account for these pebbles being dropped into the Indian deposits. Finally, it is remarked that the so-called Upper Carboniferous deposits of India and the Permian deposits of the Midlands of Britain may be practically contemporaneous, as maintained by the late Mr. H. F. Blanford, indicating a possible simultaneous existence of glaciers in England, India, and Australia.

June 20th.—Dr. Henry Woodward, F.R.S., President,  
in the Chair.

The following communications were read :—

1. 'On Deep Borings at Culford and Winkfield, with Notes on those at Ware and Cheshunt.' By W. Whitaker, Esq., B.A., F.R.S., F.G.S., and A. J. Jukes-Browne, Esq., B.A., F.G.S.

The four borings are described in detail, so far as the specimens examined would permit; these were few in the case of Culford, but many from the other borings. The following is an abstract of the formations traversed in each :—

	Culford.	Winkfield.	Ware.	Cheshunt.
	ft.	ft.	ft.	ft.
Surface Beds .....	6	—	17	14½
London Clay .....	—	136	—	30
Reading and Thanet Beds .	—	78	—	46½
Upper Chalk .....	383	329	? 183	? 273
Middle Chalk .....		177	227	? 237
Lower Chalk .....	143	219	173	183
Upper Greensand .....	—	31	40	44
Gault .....	73	264	166½	153½
Lower Greensand .....	32½	9	—	—
Palæozoic Rocks .....	19¾	—	35	29½
	657¼	1243	841½	1011

The interest of the Culford boring centres in its striking the Palæozoic floor at the small depth of 637½ feet; but the age of the slaty rocks cannot be determined. Although only 20 miles east of Ely, no Jurassic rocks exist and the Lower Cretaceous series is only about 32 feet thick, the beds differing greatly from those of Cambridgeshire but resembling those of the same age in the Richmond boring.

The Winkfield boring (3½ miles W.S.W. of Windsor) is remarkable for having been successful in obtaining water from the Lower Greensand, and for the great depth (1243 feet) to which it was carried for this purpose, the Gault being unusually thick.

The boring at Ware is now for the first time described in detail, and former accounts are corrected from specimens preserved by the New River Company. By this means, and with the assistance of Mr. W. Hill, the authors are able to give a fairly complete account of the rocks and to determine the limits of the divisions of the Upper Cretaceous Series. They deny the existence of Lower Greensand at this locality.

Of the boring at Cheshunt a more complete account is now given, based on information and specimens supplied by Mr. J. Francis, the Engineer of the New River Company.

The paper concludes with a tabular view of all the borings in the East of England, showing the level below Ordnance datum at which the Palæozoic floor occurs in each.

2. 'The Bargate Beds of Surrey, and their Microscopic Contents.' By Frederic Chapman, Esq., F.R.M.S.

3. 'On Deposits from Snowdrifts, with Special Reference to the Origin of the Loess and the Preservation of Mammoth-remains.' By Charles Davison, Esq., M.A., F.G.S.

4. 'Additions to the Fauna of the *Olenellus*-zone of the North-west Highlands.' By B. N. Peach, Esq., F.R.S., F.G.S.

5. 'Questions relating to the Formation of Coal-Seams, including a New Theory of them: suggested by Field and other Observations made during the past decade on both sides of the Atlantic.' By W. S. Gresley, Esq., F.G.S.

6. 'Observations regarding the Occurrence of Anthracite generally, with a New Theory as to its Origin.' By W. S. Gresley, Esq., F.G.S.

After discussing Dr. J. J. Stevenson's theory of the origin of anthracite, the author describes the nature and mode of occurrence of the anthracites of Pennsylvania, and gives his reasons for concluding that the de-bituminization of coal was not produced by dynamic metamorphism during mountain-building, but rather by previously applied hydrothermal action. He further discusses the applicability of his theory to other cases of anthracite, including that of South Wales and Ireland.

7. 'The Igneous Rocks of the Neighbourhood of Builth.' By Henry Woods, Esq., M.A., F.G.S.

In south-west Radnorshire (just north of Builth) there is an area of Ordovician and associated igneous rocks, surrounded on all sides except the north-west by Silurian beds; this is shown on Sheets 56 S.W. and S.E. of the Geological Survey map, and was described by Murchison. In this paper the author gives a map of the southern half of this area, and a description of the igneous rocks—andesites, andesitic ash, rhyolites, diabase-porphyrity, and diabase. The diabase-porphyrity is intrusive in the andesite, and the diabase in the Llandeilo Shales. The andesitic ash rests on the andesite, and is overlain by the Llandeilo Shales. The author concludes that the andesites, andesitic ash, rhyolites, and diabase-porphyrity are of Lower Llandeilo age; and that the diabases are post-Llandeilo and pre-Llandovery.

8. 'On the Relations of some of the Older Fragmental Rocks in North-west Caernarvonshire.' By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S., and Miss Catherine A. Raisin, B.Sc.

In a recent paper on 'The Felsites and Conglomerates between Bethesda and Llanllyfni, North Wales,' it is argued that, in the well-known sections on either side of Llyn Padarn, a great unconformity separates the rocks into two totally distinct groups.

The authors of the present communication discuss at the outset the great physical difficulties involved in this hypothesis; a subject

which, in their opinion, was passed over too lightly by the author of that paper.

They further affirm, in the course of a description of the sections, which are most clear and afford the best evidence :—

(1) That the strike in both the supposed rock-groups is generally similar.

(2) That the same is true of the dips.

(3) That very marked identity of lithological characters may be found in rocks on either side of the alleged unconformity, specimens occasionally being practically indistinguishable.

(4) That in no case, which has been examined, can any valid evidence be found in favour of the alleged unconformity, and that in the one which is supposed to be the most satisfactory proof of it the facts are wholly opposed to this notion.

## LXIX. *Intelligence and Miscellaneous Articles.*

### ON THE ENERGY OF THE AMPERIAN MOLECULE.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

WITH reference to the paper by Mr. Fawcett and myself published in your last issue, Prof. Oliver Lodge has kindly sent me the following interesting considerations.

If temperature is due solely to translational and vibrational motions of molecules, it is possible that an appreciable time may be required before the sudden alteration of the rates of rotation of the molecules of a piece of iron can cause an alteration in the temperature of a neighbouring thermopile. It follows that, if this be so, an inseparable connexion may still exist between molecular spin and molecular magnetism, in spite of our negative result.

It is true that our experiments lasted on the average from two to three minutes, and in two cases for four minutes and a half, without any marked temperature effect appearing; but an examination of our results in the light of Dr. Lodge's suggestion does certainly show that in every case (except curve *f*, where the temperature was probably changing rather rapidly) there is a very slight upward tendency of the curve after the first sudden bend is over, which is in the direction of the effect sought; and this tendency is also most conspicuous in the earlier readings (p. 477), where the time-interval was greatest.

I confess that it had not occurred to me as possible that several minutes might elapse before an alteration in the rotations of a set of molecules could make itself felt in their translational velocities, and for molecules consisting of more than one atom this still seems to me very unlikely; but if the rotations dealt with are those of single atoms spinning about their own centres, between which it is perhaps not unreasonable to assume the absence of any marked tangential forces during collision [and I take this to be the case contemplated by Dr. Lodge], there seems to be no reason why

the time of adjustment or distribution of energy among the degrees of freedom should not extend to long periods.

The difficulties connected with any considerable increase in the duration of the experiments will undoubtedly be great, as it will be necessary to maintain the temperature so very uniform; but we hope shortly to attack the problem again from this point of view.

University College, Bristol,  
November 12, 1894.

I am, Gentlemen,

Yours obediently,

A. P. CHATTOCK.

ON THE PROPAGATION OF ELECTROMAGNETIC WAVES IN ICE,  
AND ON THE DIELECTRIC POWER OF THIS SUBSTANCE. BY  
M. BLONDLOT.

In a previous note (*Comptes Rendus*, July 25, 1892) I enunciated the following proposition:—The length of the waves which an electromagnetic oscillation can emit is the same whatever be the insulating medium in which the experiment is made; in other words, the wave-length depends on the oscillator alone, just as in acoustics the wave-length of a pipe depends only on the length of the pipe.

The confirmatory experiments described in the Note cited referred to oil of turpentine and to castor-oil; the law holds perfectly for both these substances, and everything leads to the belief that this will be the same for other dielectrics.

There is, however, a doubt about ice, in consequence of the exceptional properties ascribed to it. The experiments of M. Bouty (*Comptes Rendus*, March 7, 1892) show in fact that ice has a dielectric power of 27, that is to say incomparably greater than that of all other substances. Suspecting that the law relative to the propagation of waves might not apply to a dielectric so different from the others, I resolved to submit the question to experiment.

For these investigations I availed myself of the intense and prolonged frosts of the winter of 1892-93. M. M. Dufour has helped me in carrying them out, which the rigour of the cold rendered difficult and even painful. I thank him for his extreme kindness on this occasion.

The method which I adopted was the following, which, with slight modifications necessitated by the solid character of the dielectric, is the same as that I used in the case of turpentine and castor oil.

Electromagnetic waves were transmitted along two tinned copper wires 2·5 millim. in diameter, stretched horizontally and parallel to each other at a distance of 0·8 metre. A resonator of gilt copper is placed in a fixed position between the wires; the portion of the transmitting wires beyond the resonator is contained in a wooden trough 4 metres in length. The trough being filled with liquid, the position is sought at which a movable bridge must be placed joining the wires beyond the resonator to cause the spark to disappear; the distance from the bridge to the resonator is then

a quarter of the specific wave-length of the resonator; the position of the bridge is accurately noted.

That done, I surround the part of the resonator forming the condenser with a watertight bag of parchment-paper which I fill with distilled water, and then freeze this water; the layer of air is thus replaced by one of ice. Measuring the wave-length afresh, it is found to be considerably greater than in the first experiment, having become  $\frac{141}{100}$  of what it was.

The trough is then filled with water which is frozen, and then the position of the bridge for disappearance of the spark is again sought. For this purpose the ice at the distant end of the trough is broken and progressively removed. I ascertained that this position is *exactly* the same as in the first case, when the dielectric was air.

The experiment four times repeated, varying each time the capacity of the condenser, always gave the same result. The proposition relative to the wave-length is therefore true for ice as well as for other dielectrics. Hence, as shown in my previous Note, Maxwell's relation that the dielectric power is also equal to the square of the refractive index also holds for electromagnetic waves in the case given.

The preceding results, partly unforeseen, led me to determine the dielectric constant of ice, using electromagnetic undulations. The experiment cited above gave all the data necessary for this determination.

For if  $\lambda$  and  $\lambda_1$  are the wave-lengths corresponding to a given resonator, working respectively in air and in a substance of dielectric power  $K$ , we have

$$\frac{\lambda'}{\lambda} = \sqrt{K}.$$

As stated above, I found

$$\frac{\lambda'}{\lambda} = \frac{141}{100},$$

whence

$$K=2 \text{ in round numbers.}$$

The experiment repeated a dozen times always gave the same result. I consider the relative error does not exceed  $\frac{1}{20}$ , for the plate of ice was almost entirely free from air-bubbles. According to this, ice does not present exceptional dielectric properties.

It remains to be explained how MM. Bouty and A. Perot obtained values of a totally different order for the dielectric power of ice. In the first place, in M. Bouty's method the charge and discharge were enormously slower than in my experiments. Is it not probable, then, that the physical magnitudes measured by M. Bouty and myself were in themselves very different. In any case we know at present too little about the dielectric properties of bodies to be surprised at the divergences of numbers obtained by two methods so dissimilar, however great they are.—*Comptes Rendus*, October 8, 1894.

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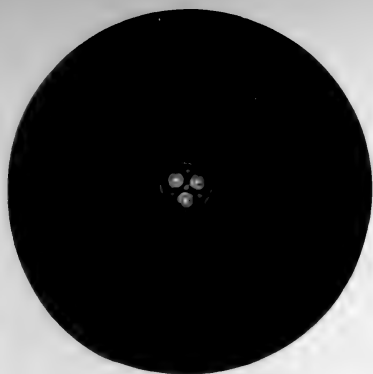


Fig. 2.

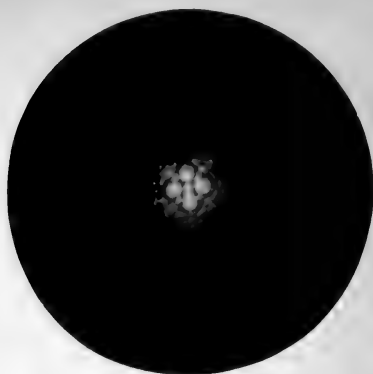


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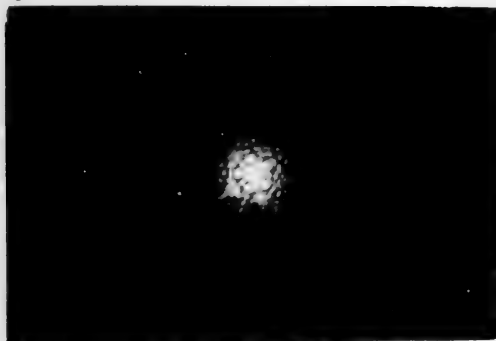


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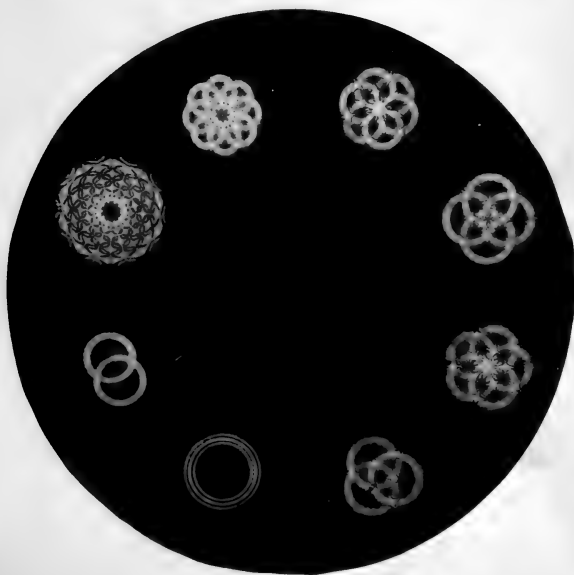


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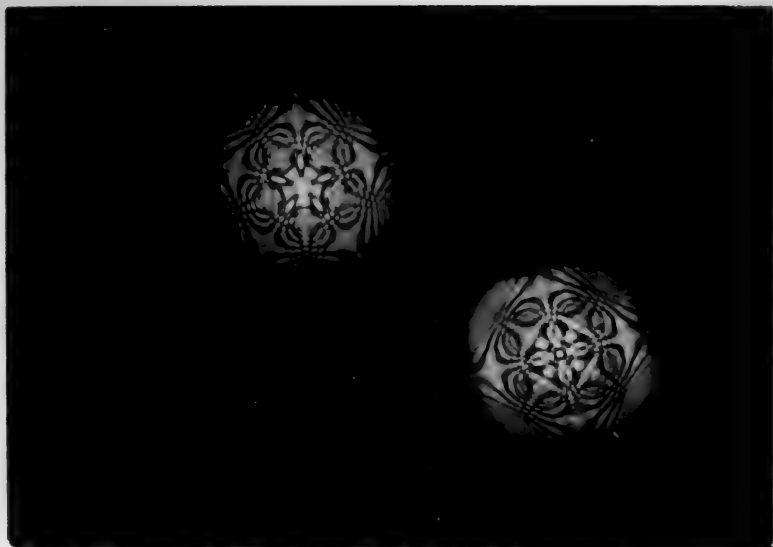


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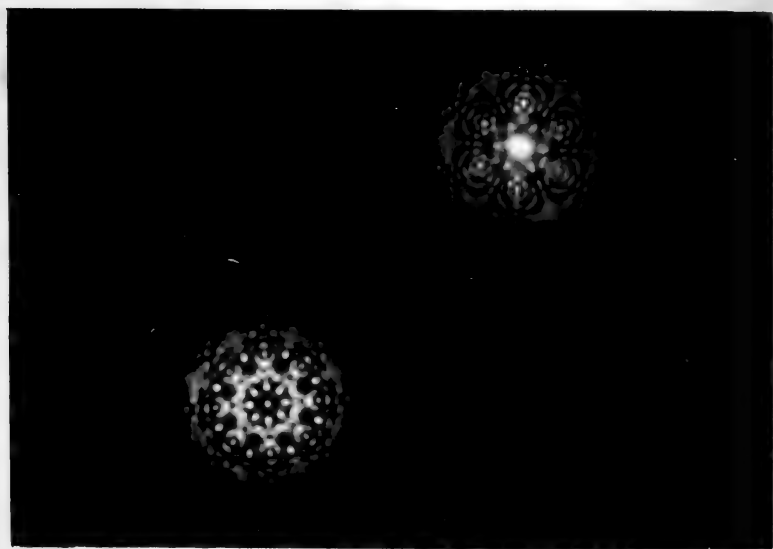


Fig. 13.





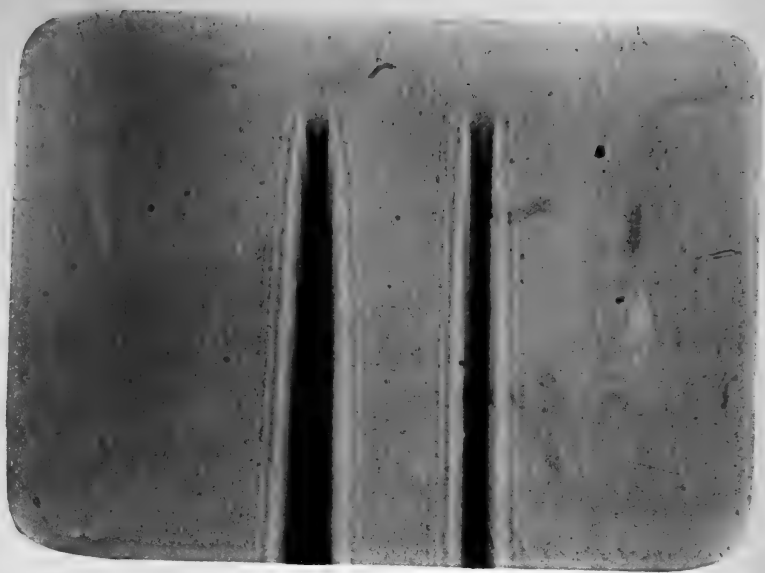


Fig. 71.



Fig. 72.



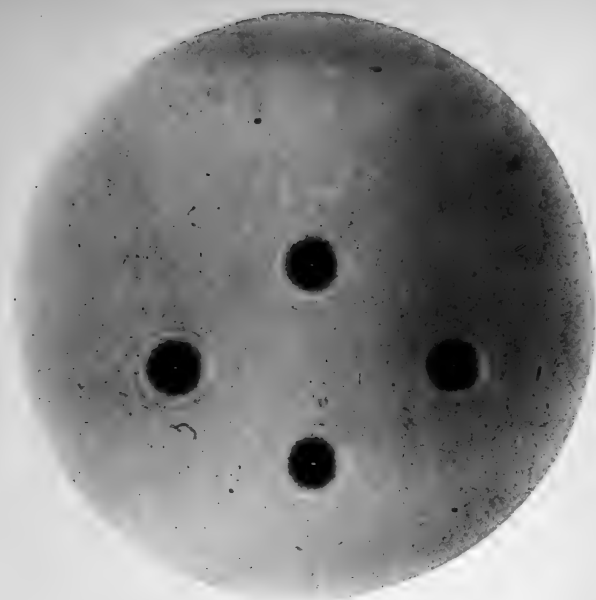


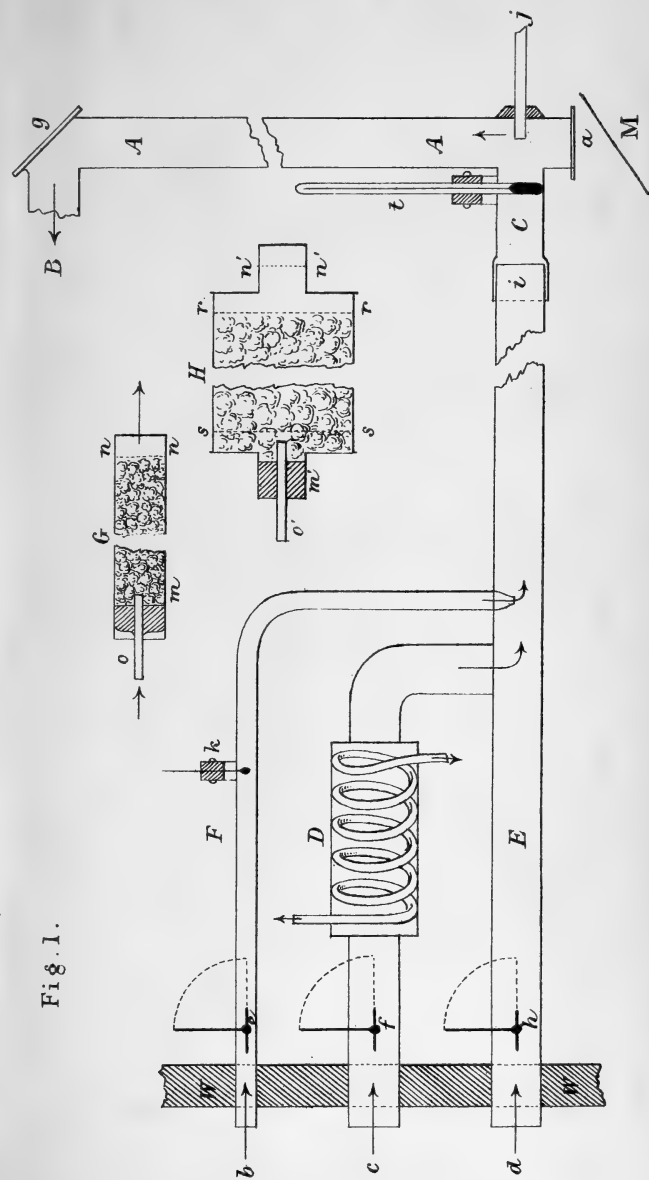
Fig. 75.



Fig. 83.



Fig. 1.



Color tube AA, with attached heater ED, duster F, and other appurtenances. G and H, filters. Sectional elevation. Diagram.









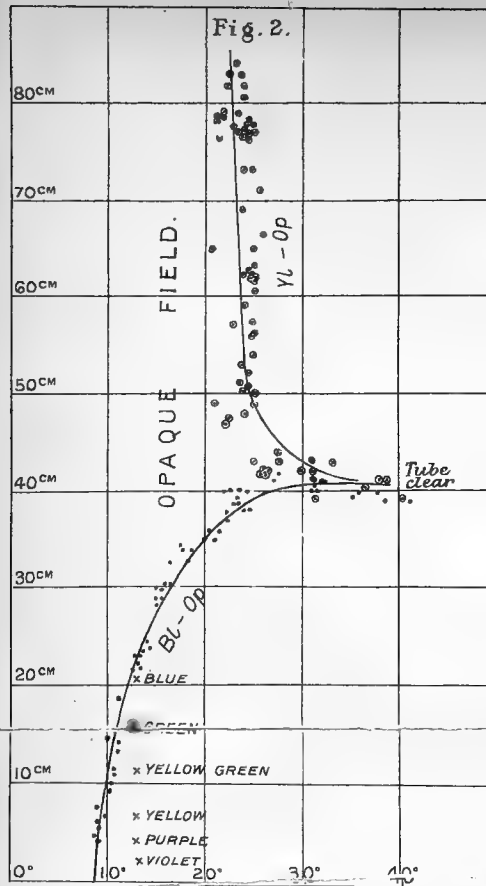


Chart showing the margins of the opaque field in terms of the actuating steam pressure and the air temperature.

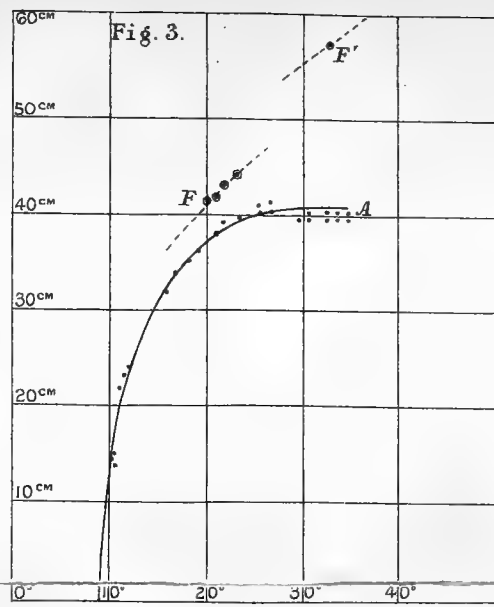


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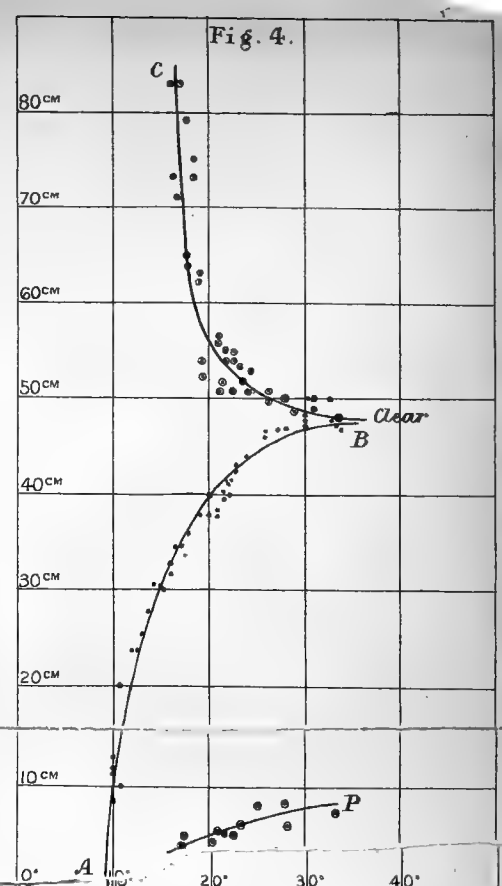


Chart showing the margins of the opaque field in terms of the actuating steam pressure and the air temperature.

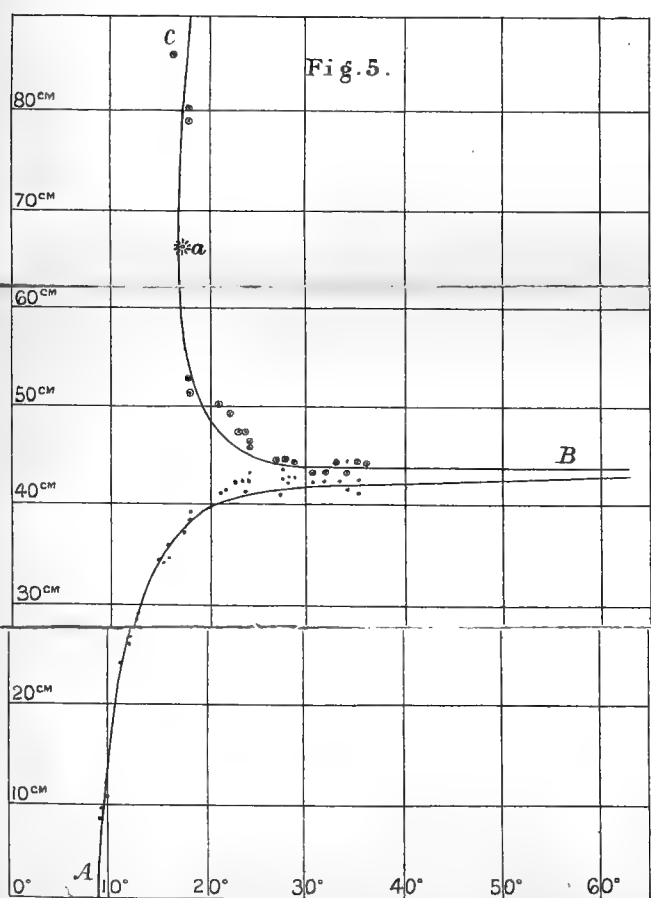
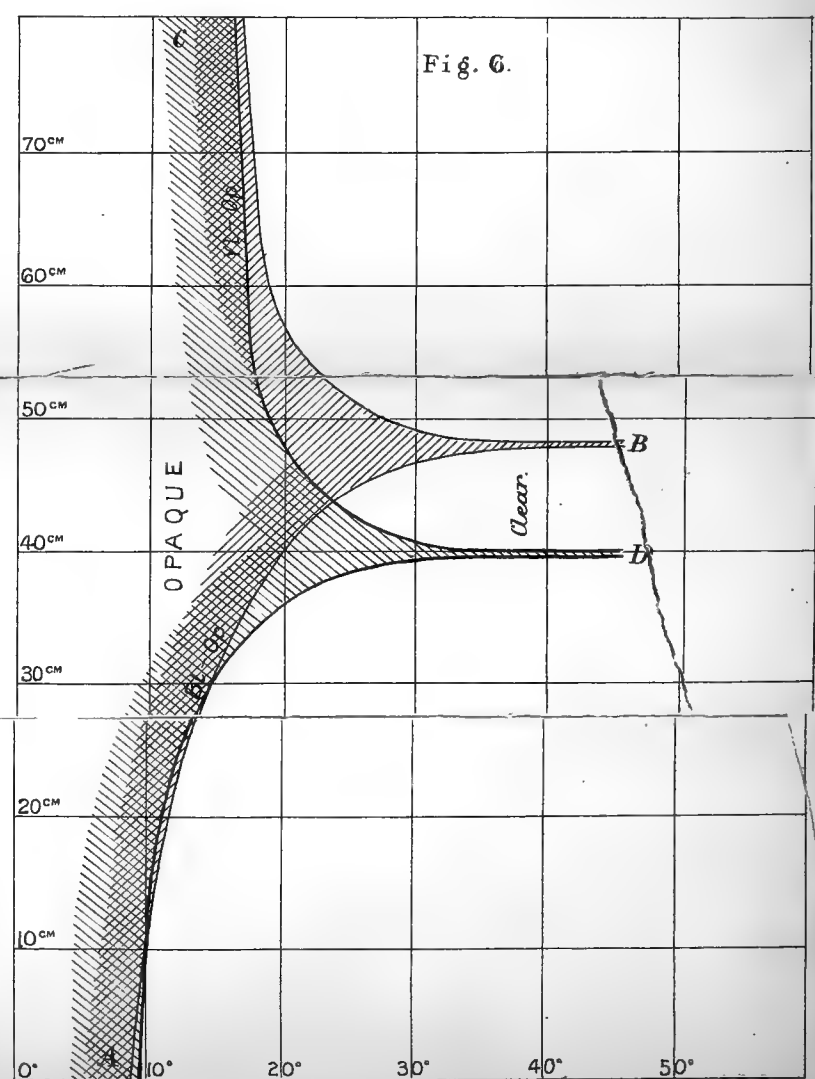


Chart showing the margins of the opaque field in terms of the actuating steam pressure and the air temperature.



Variation of the opaque margin due to a change of dust contents. Diagram.

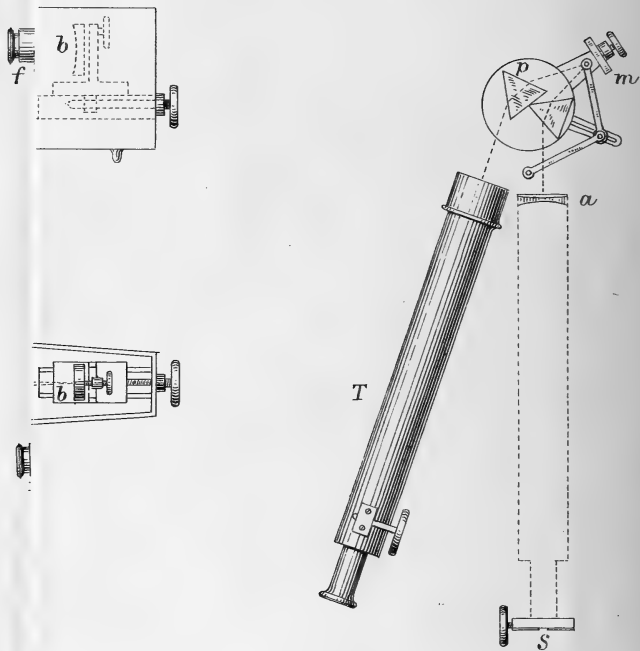


Fig. 4.

Fig. 4

S'

S





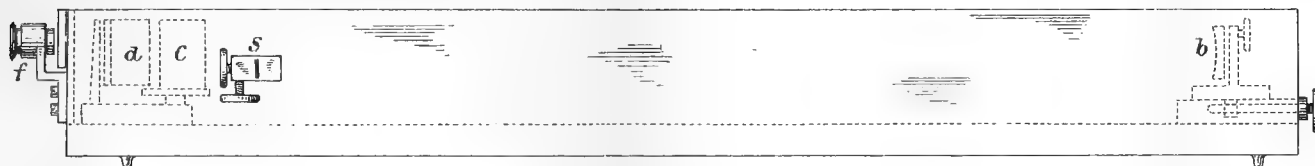


Fig. 1.

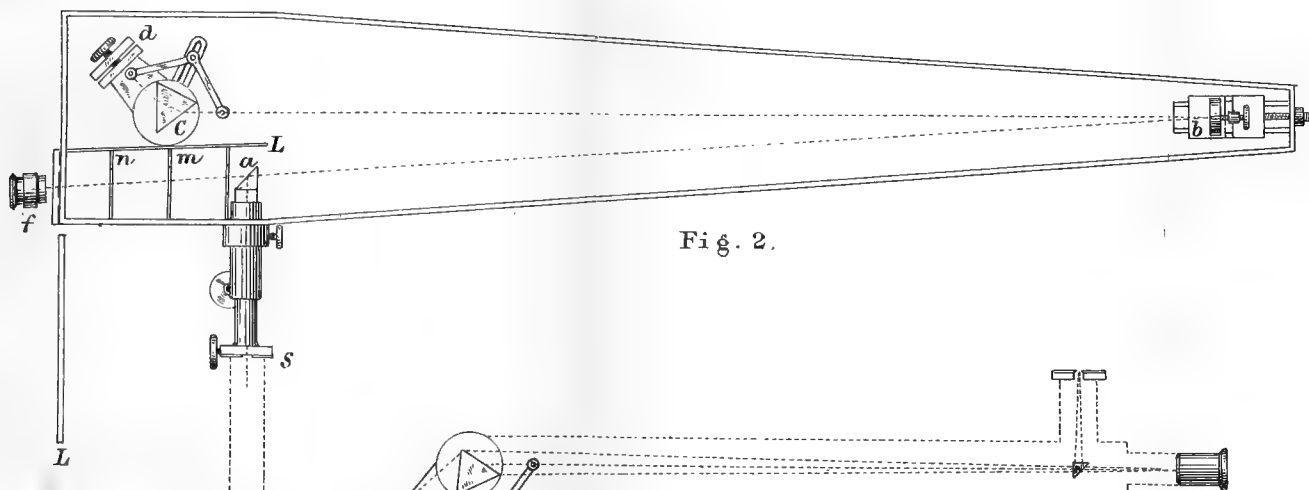


Fig. 2.

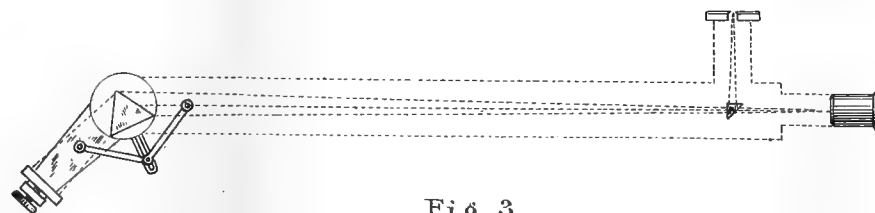


Fig. 3.

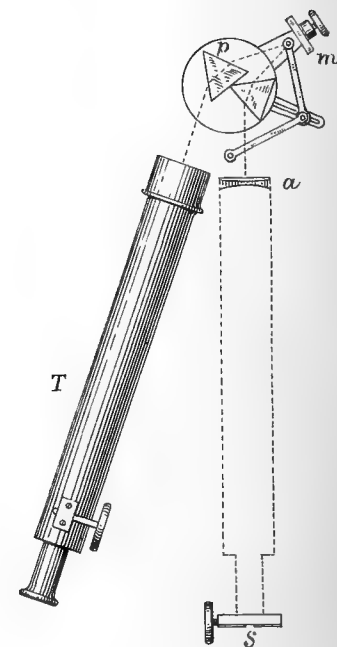


Fig. 4.



*b*



*b*



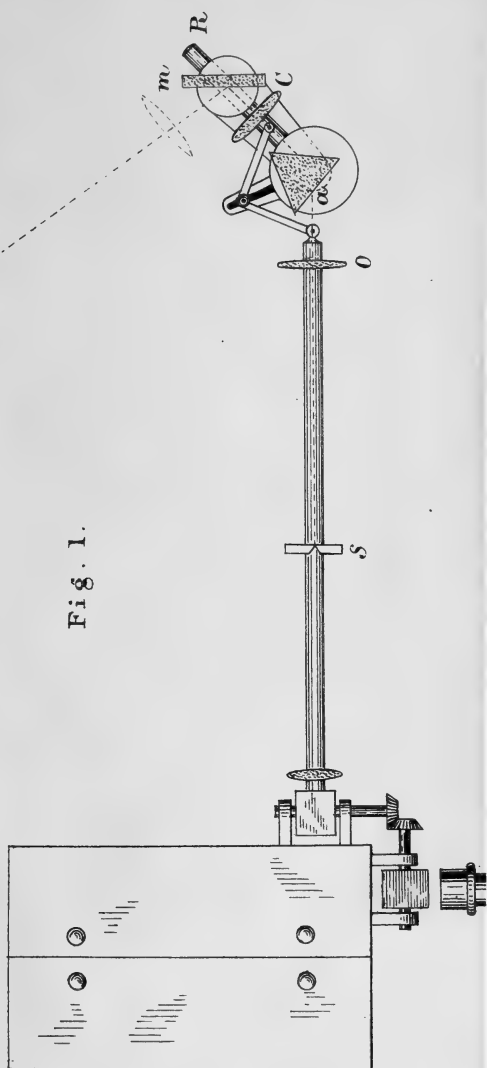


Fig. 1.

Mintern Bros. lith.





Fig. 2

S''

S'

S

Fig. 3

S''

S'

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Fig. 4

S'

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Fig. 5

S'

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Fig. 6

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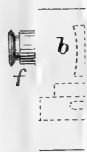
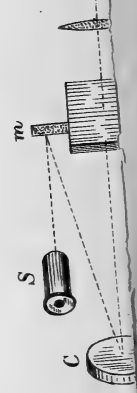
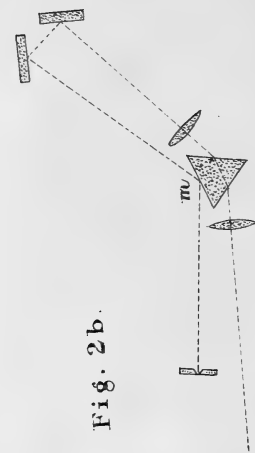


Fig. 2

Fig. 2b.



Mintern Bros. lith.



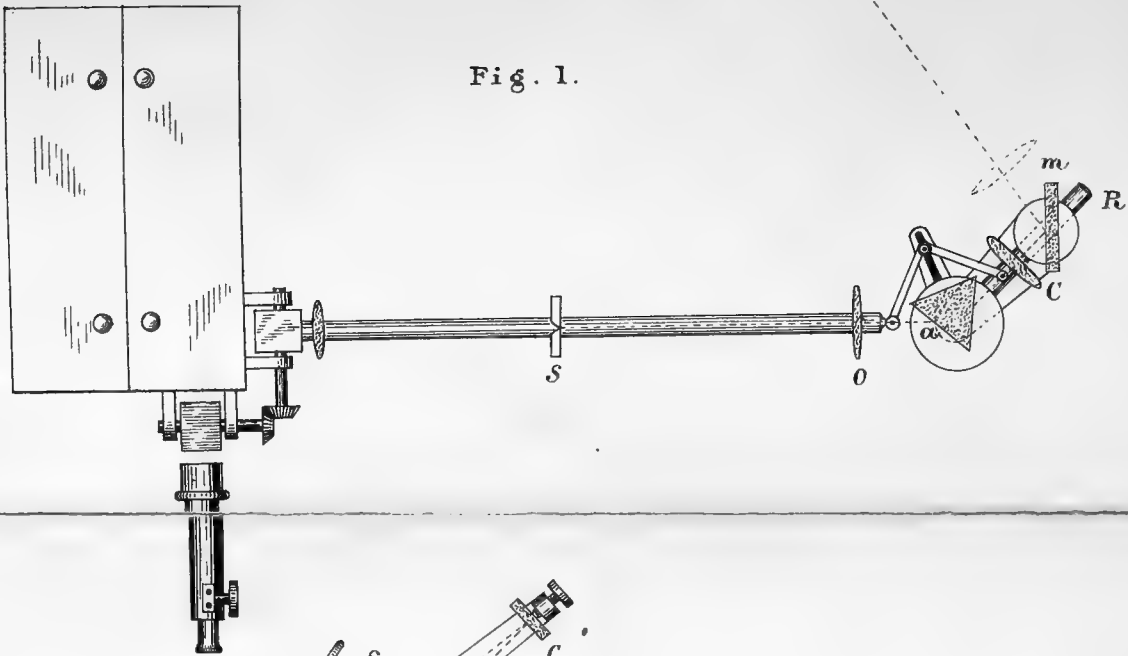


Fig. 1.

Fig. 2.

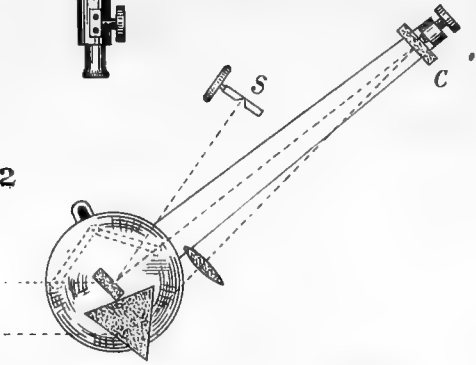


Fig. 2b.

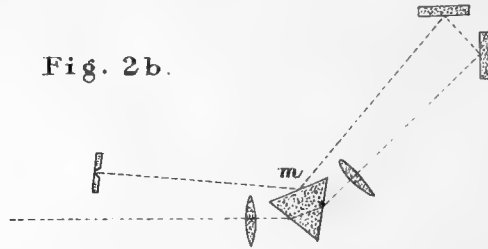
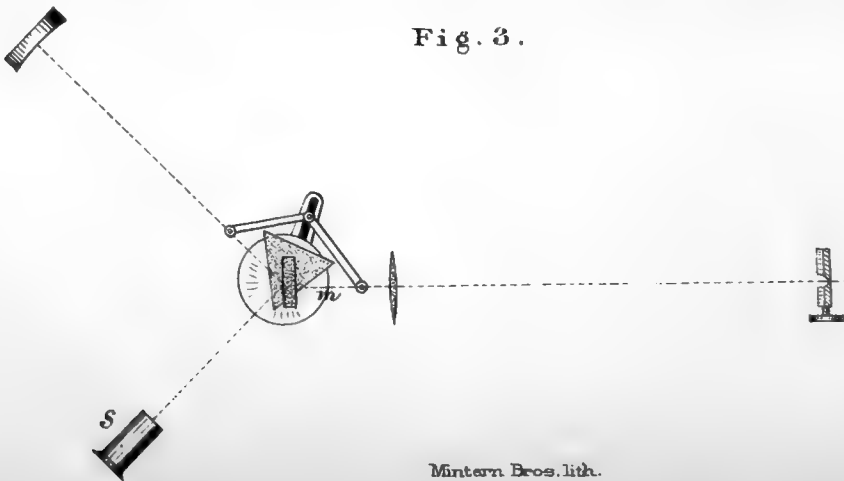
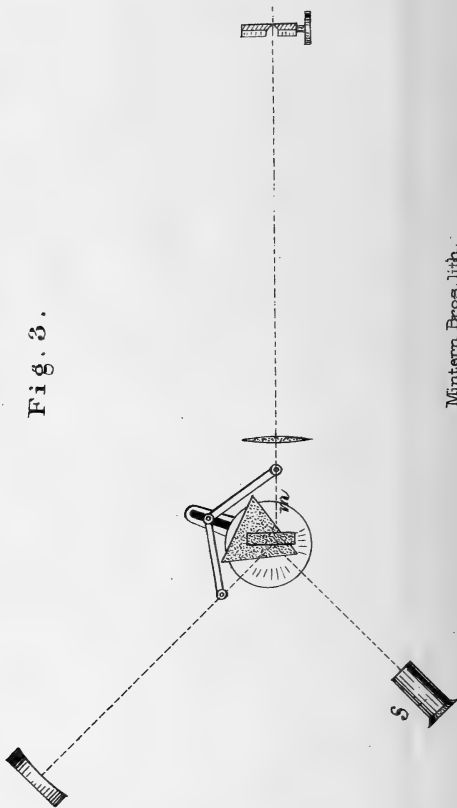


Fig. 3.



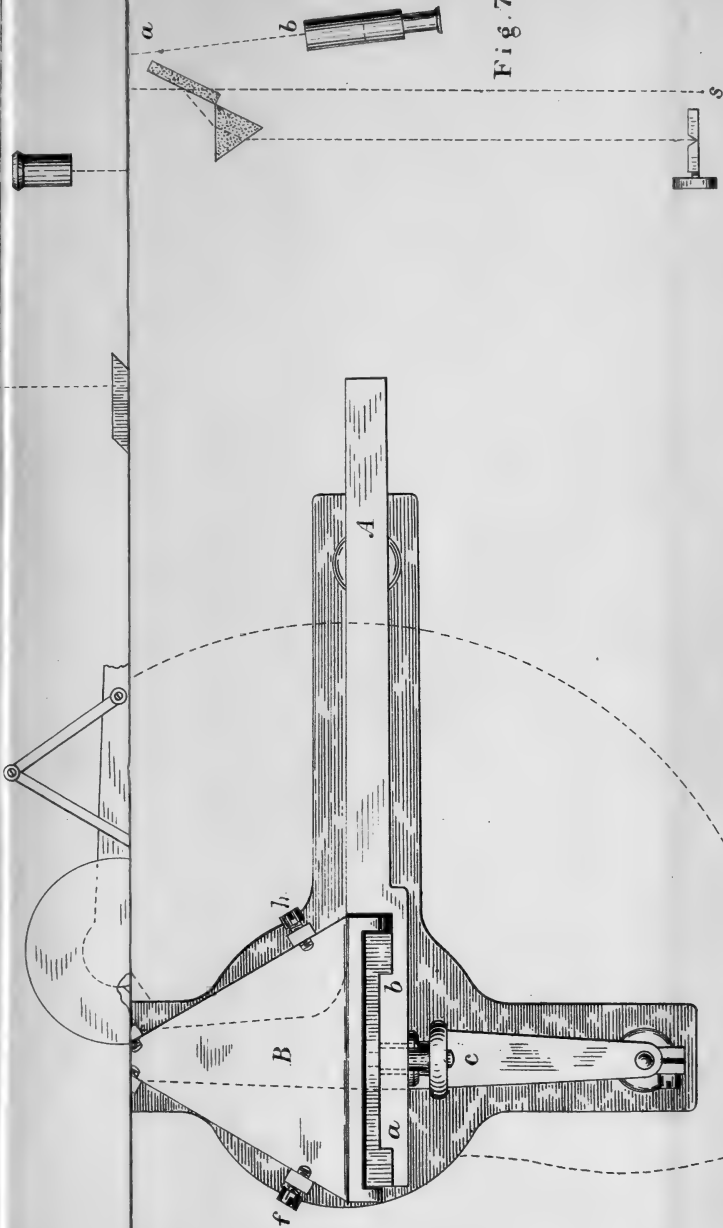
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Fig. 3.



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Fig. 7.



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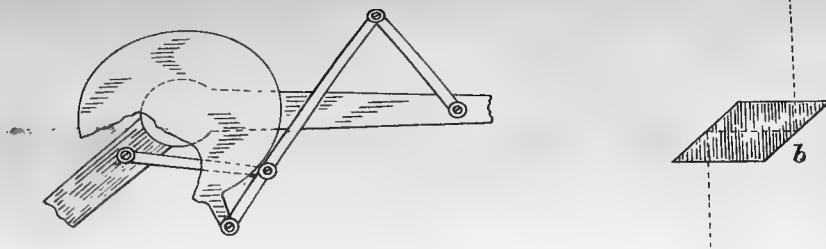


Fig. 4.

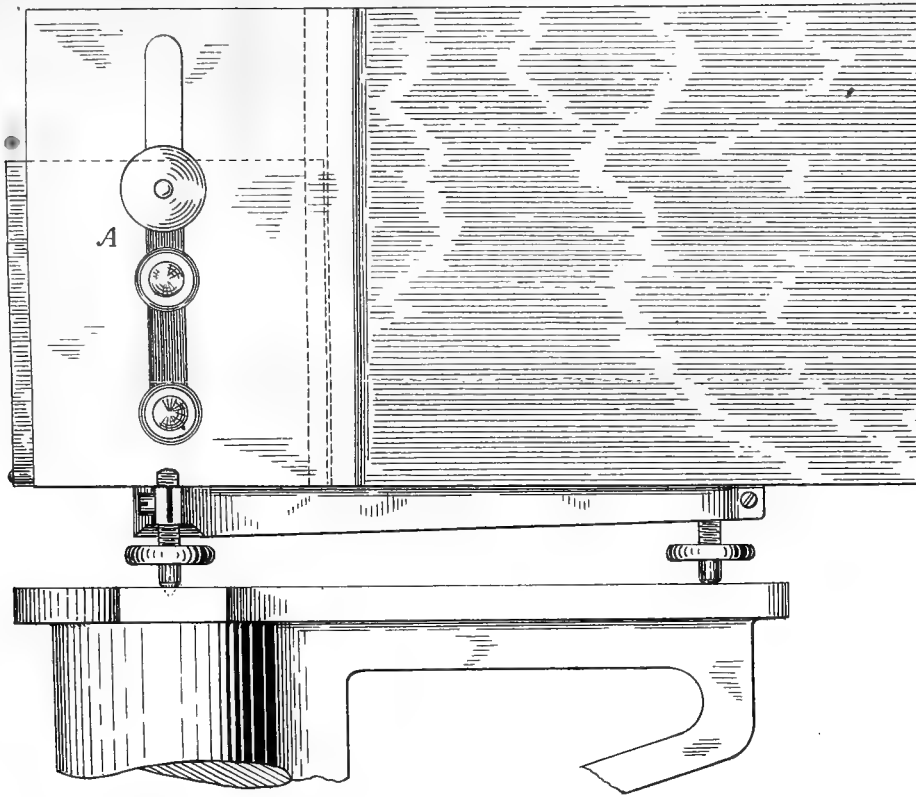


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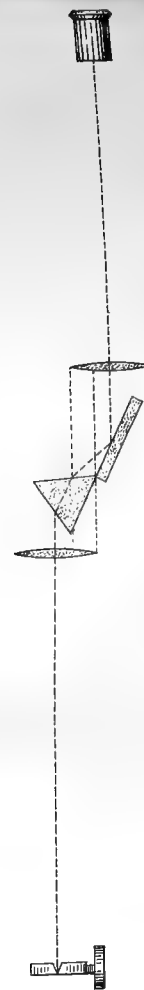
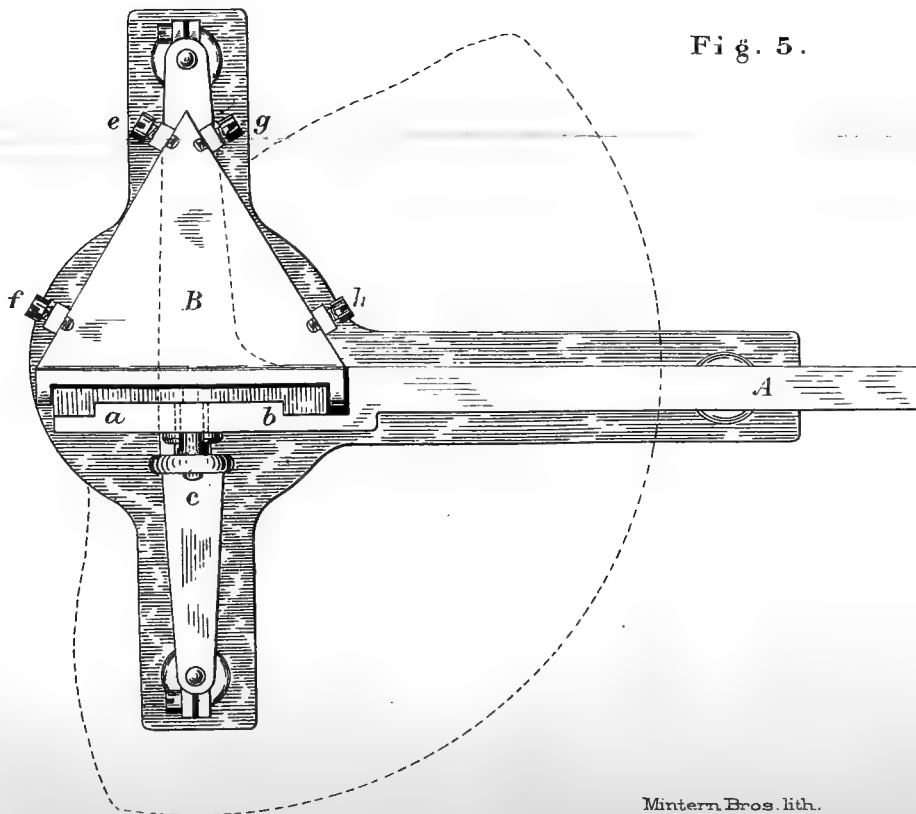


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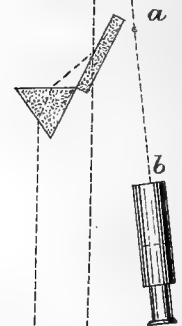
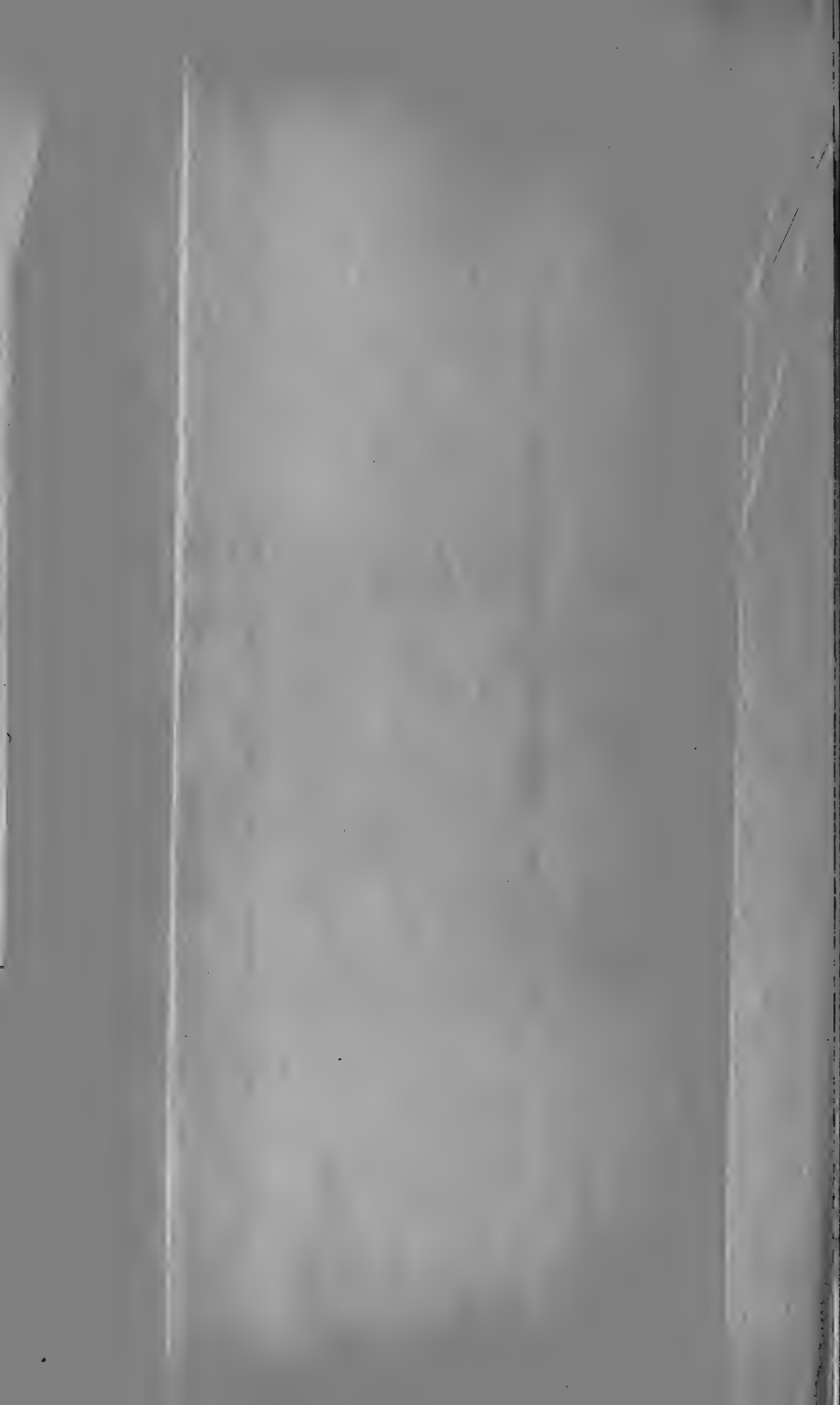
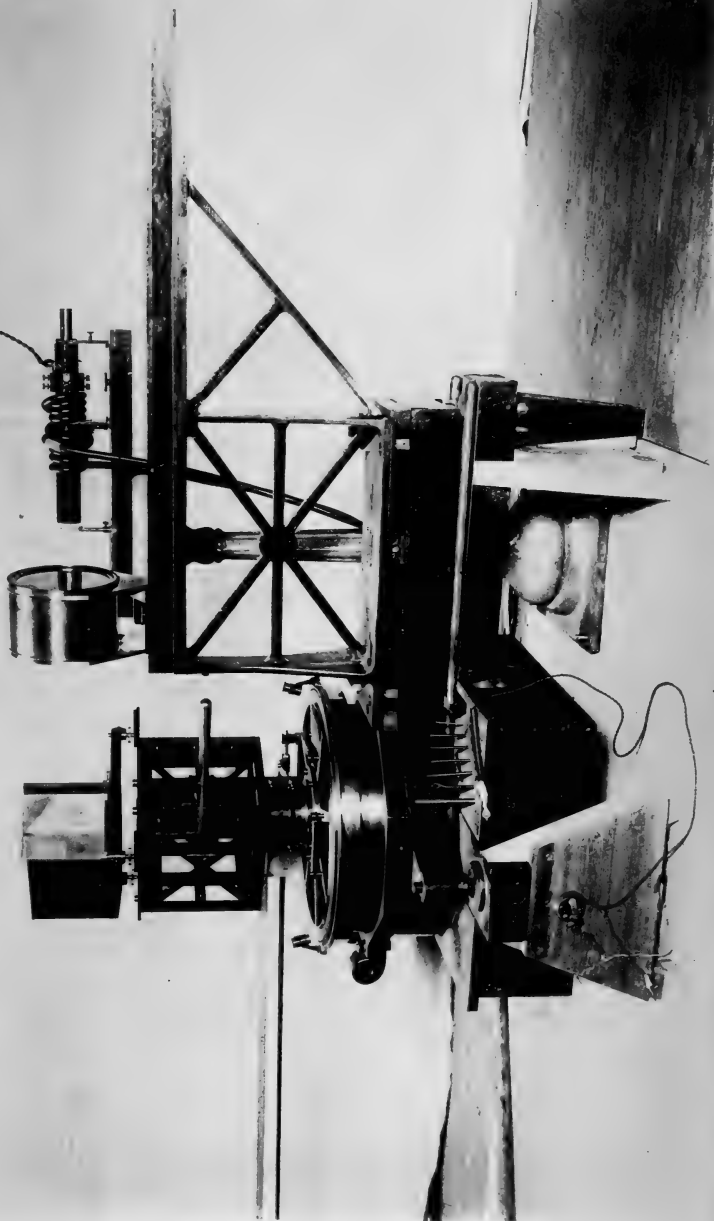
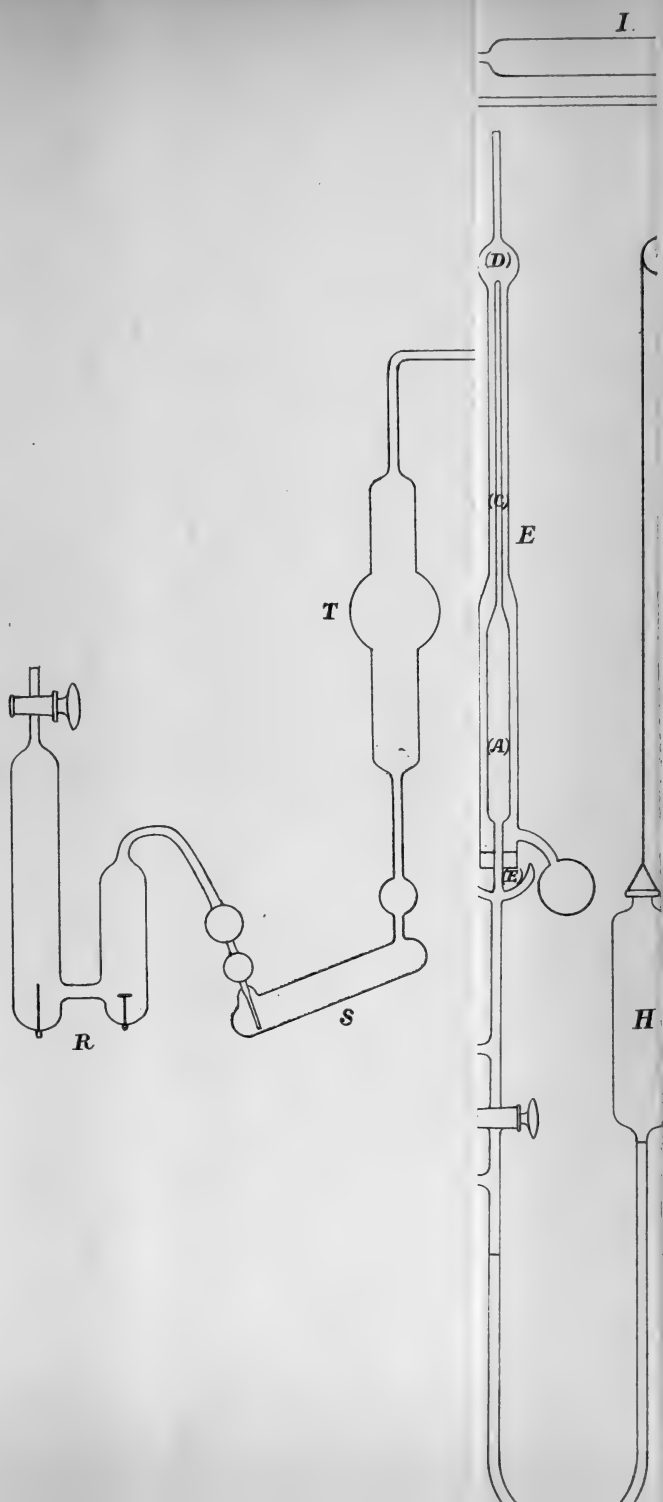


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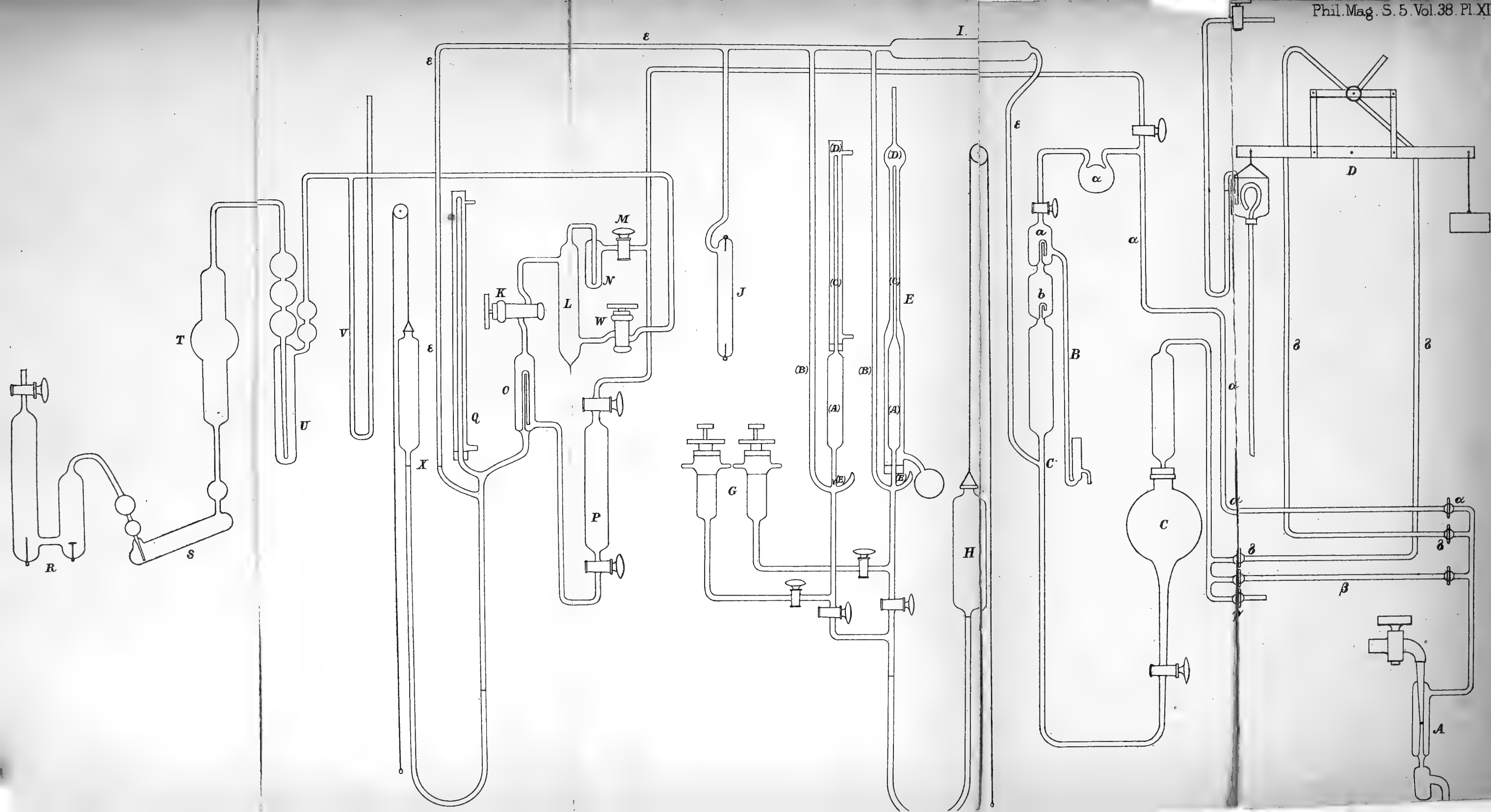






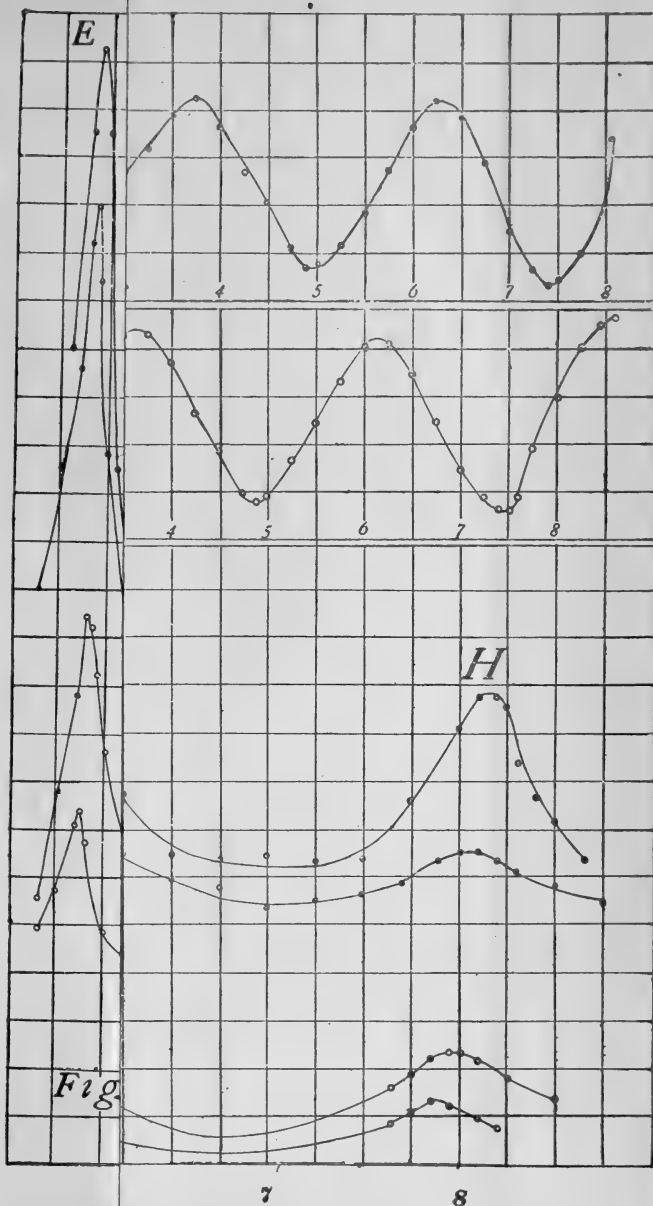




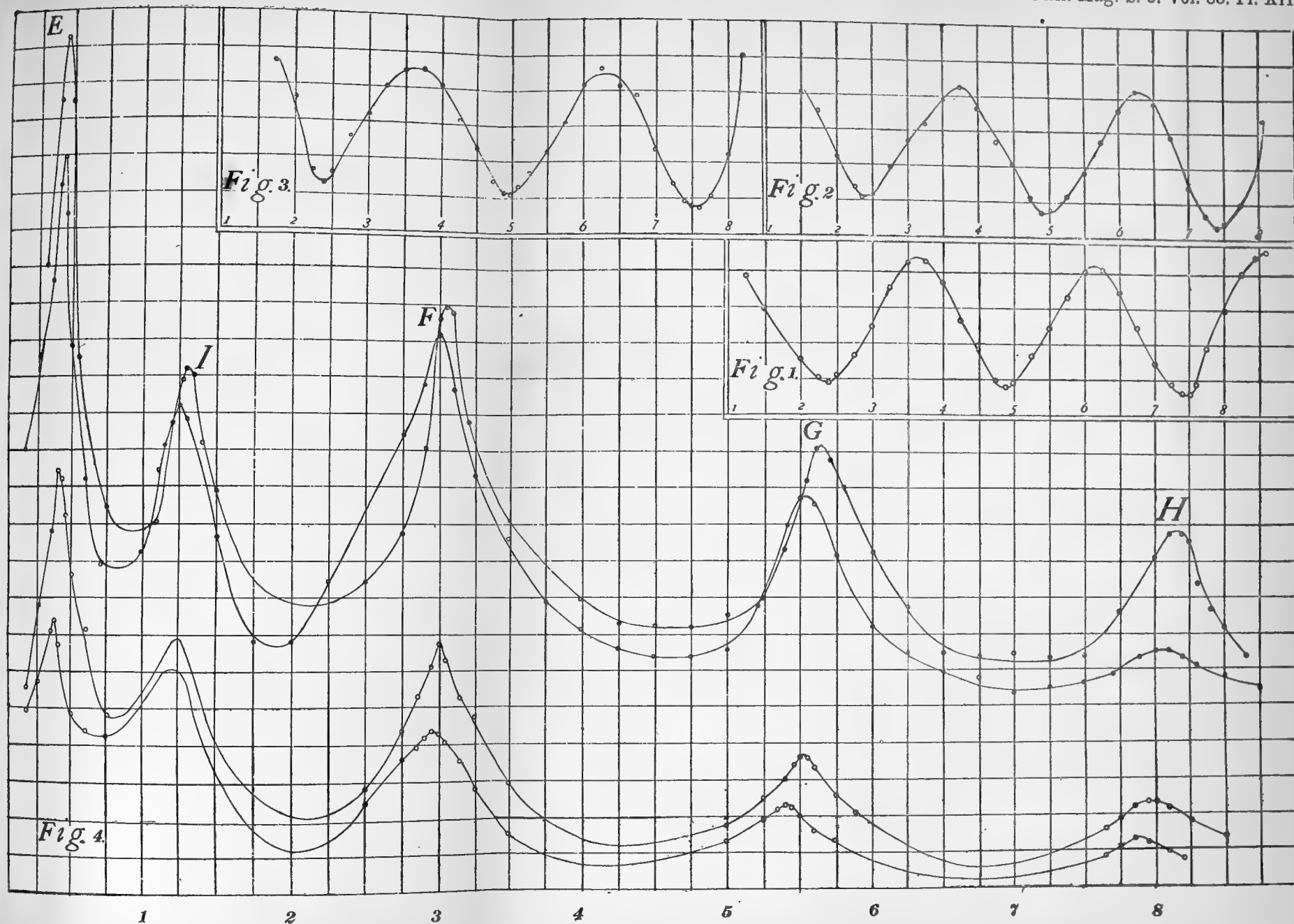


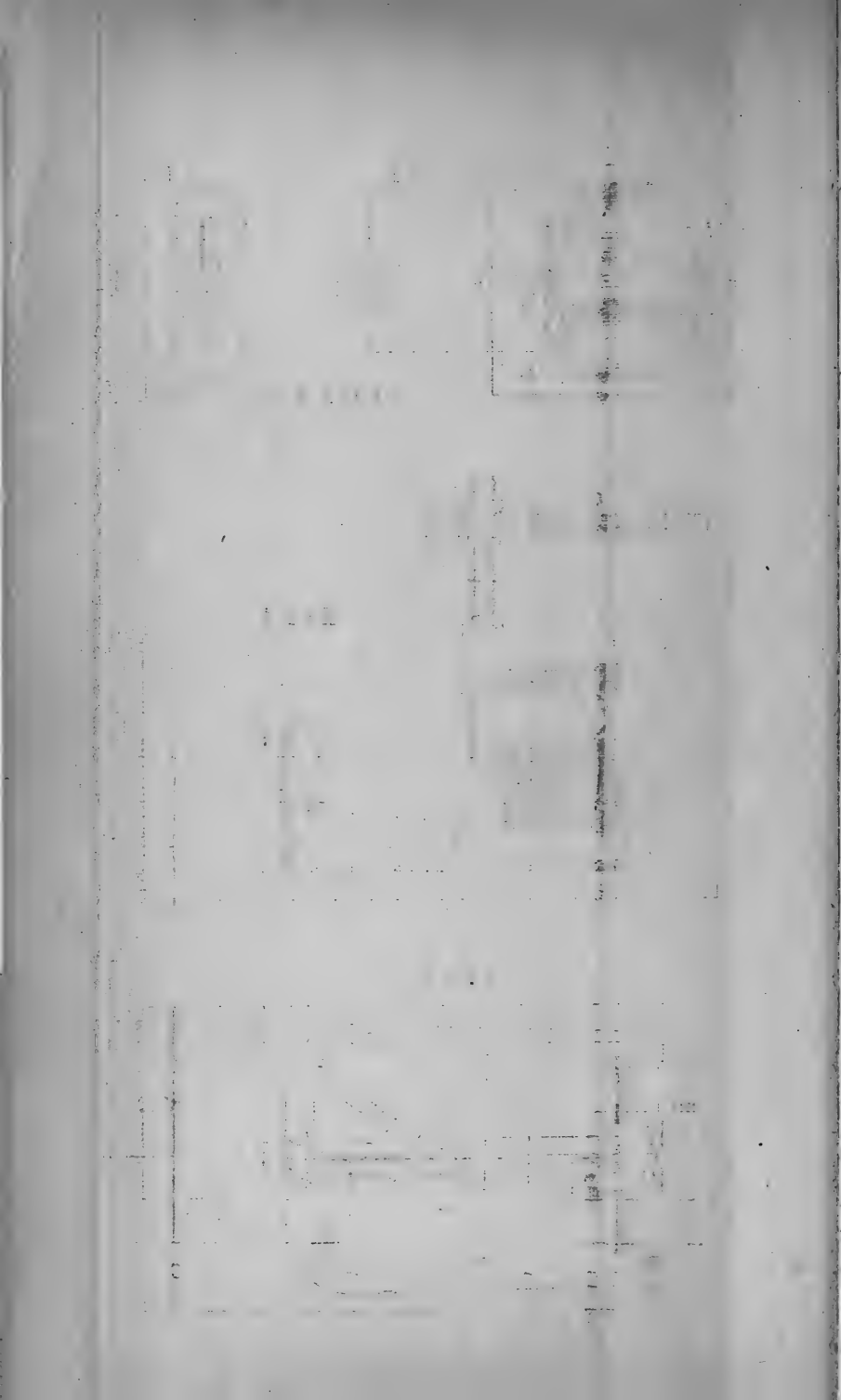


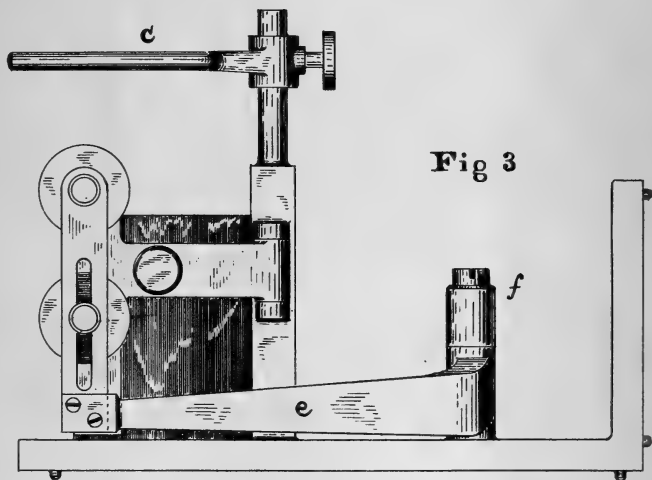
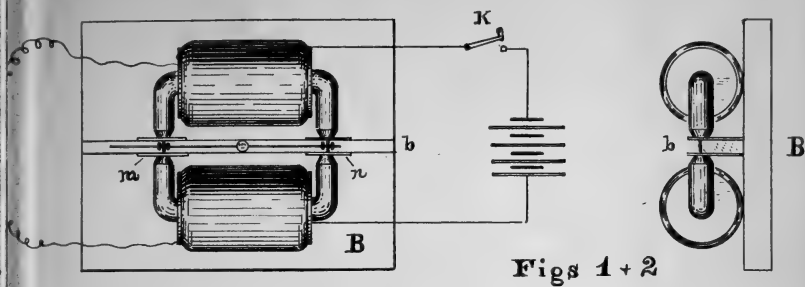




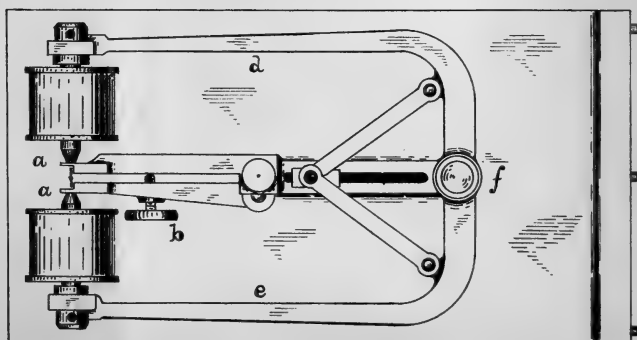




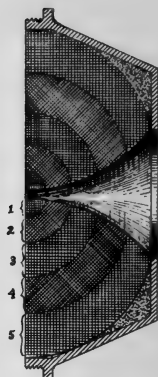
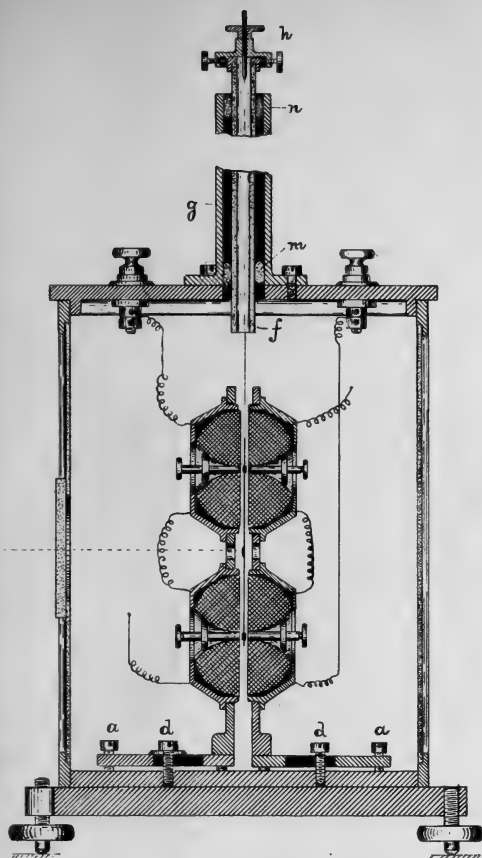




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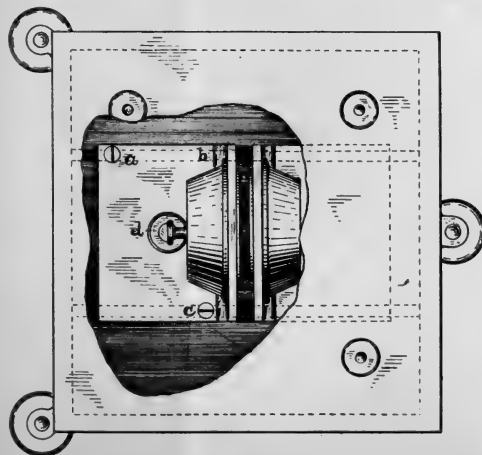






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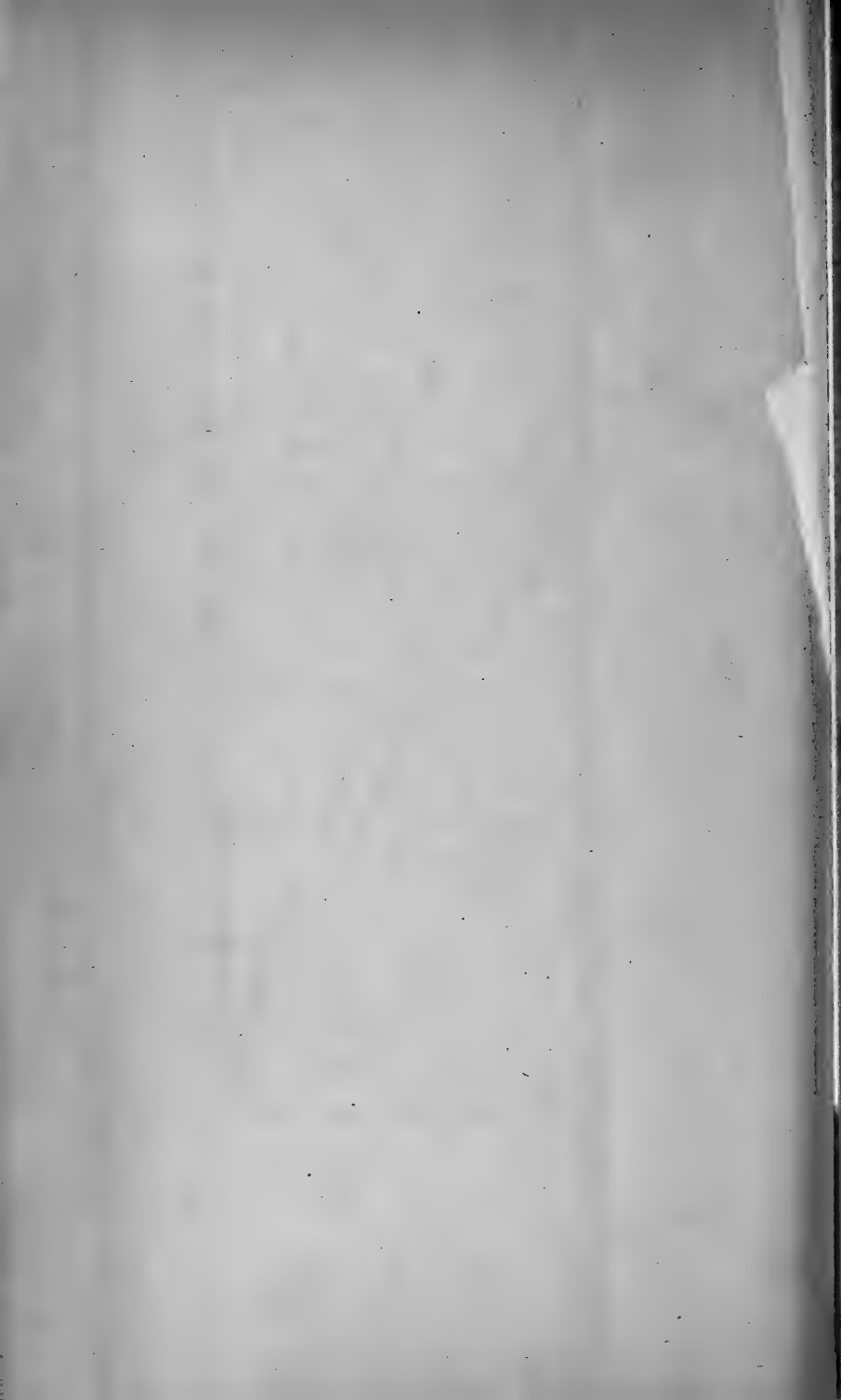
**Fig 2**



**Fig 3**



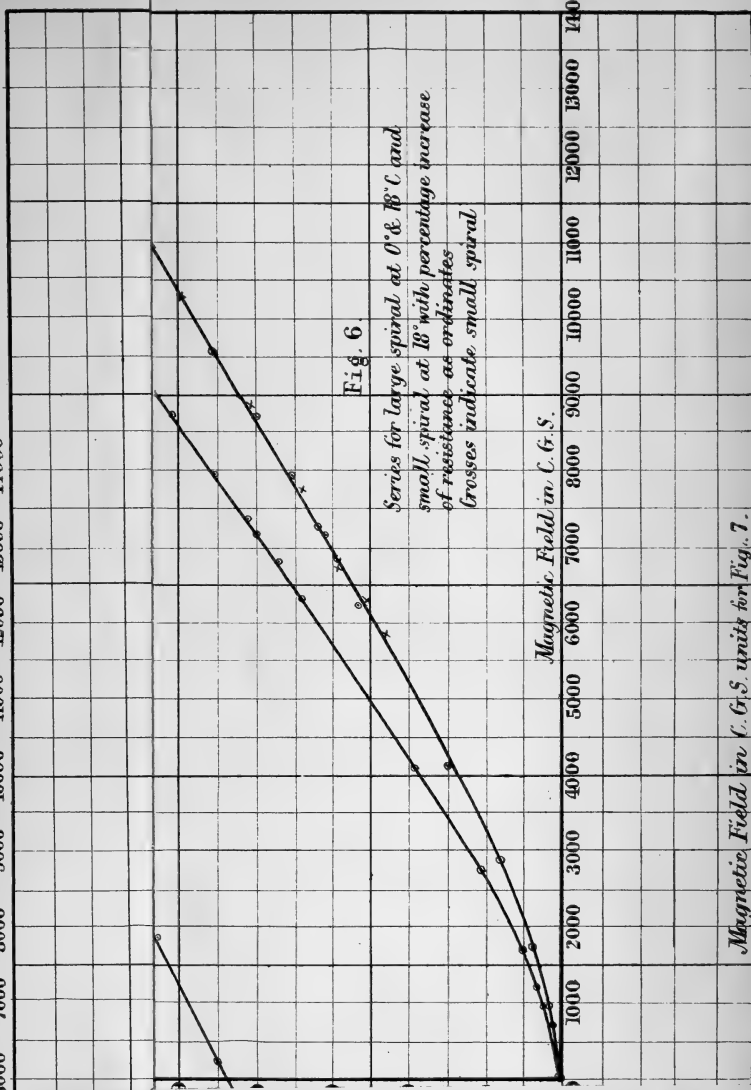
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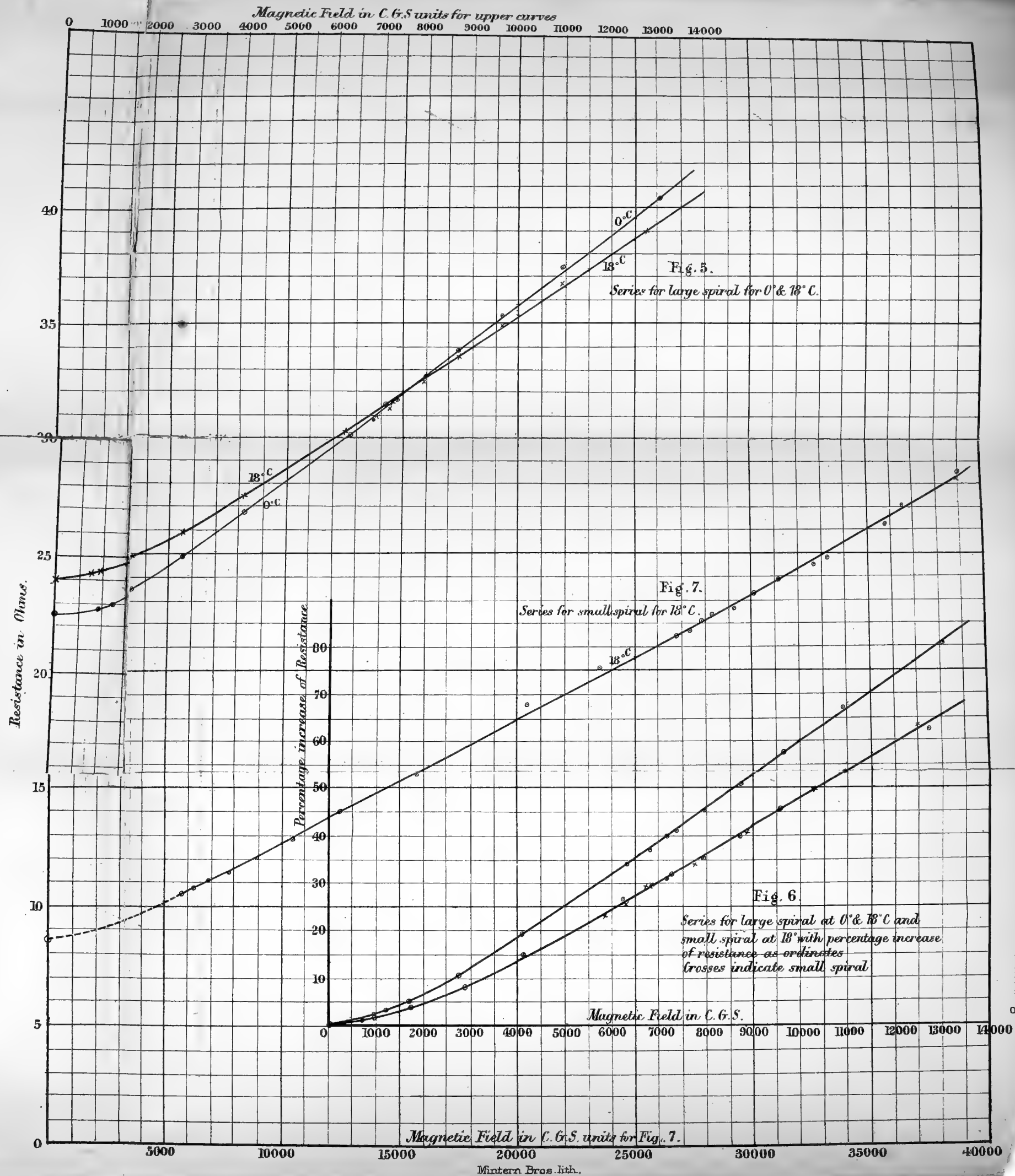


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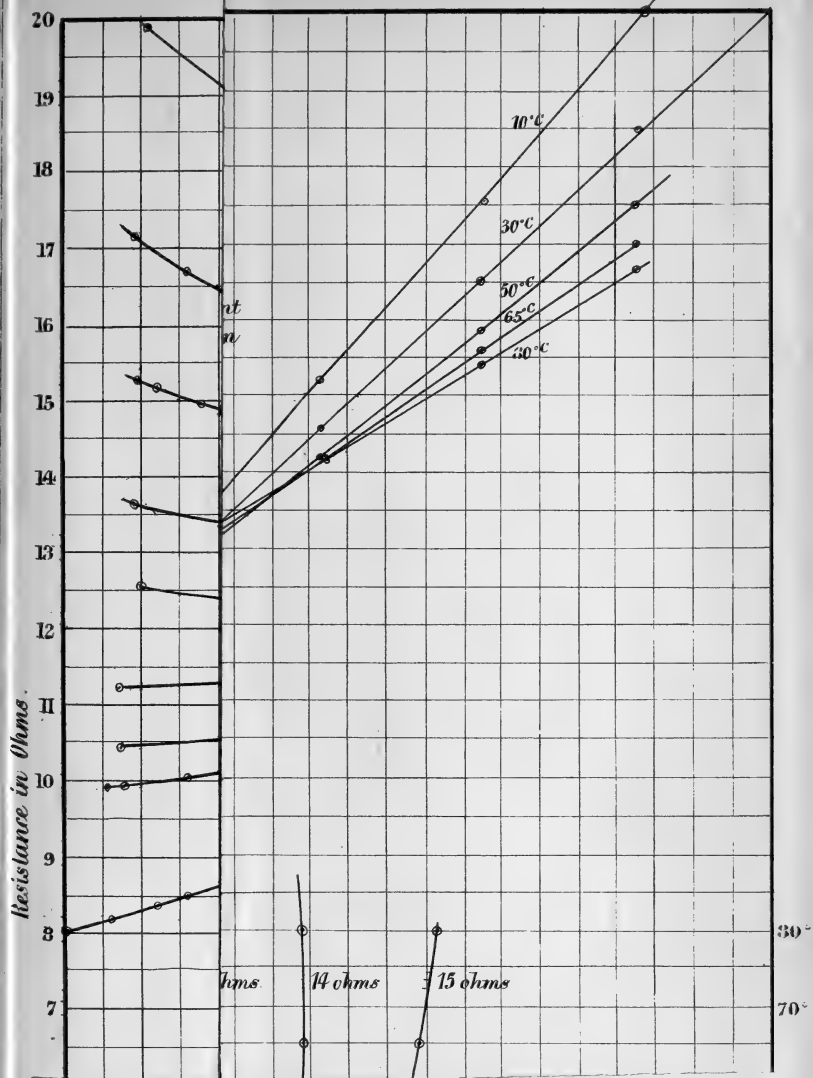
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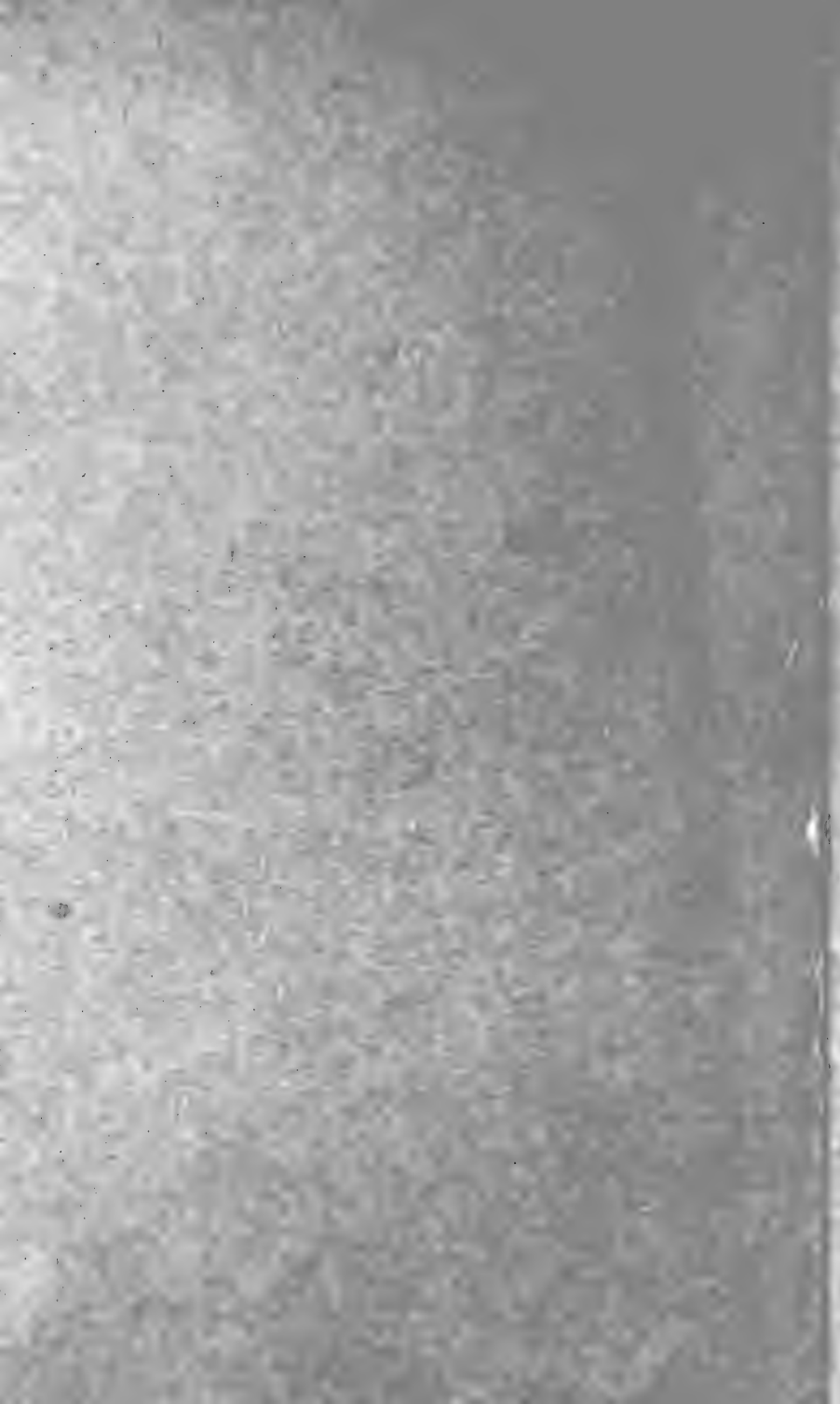


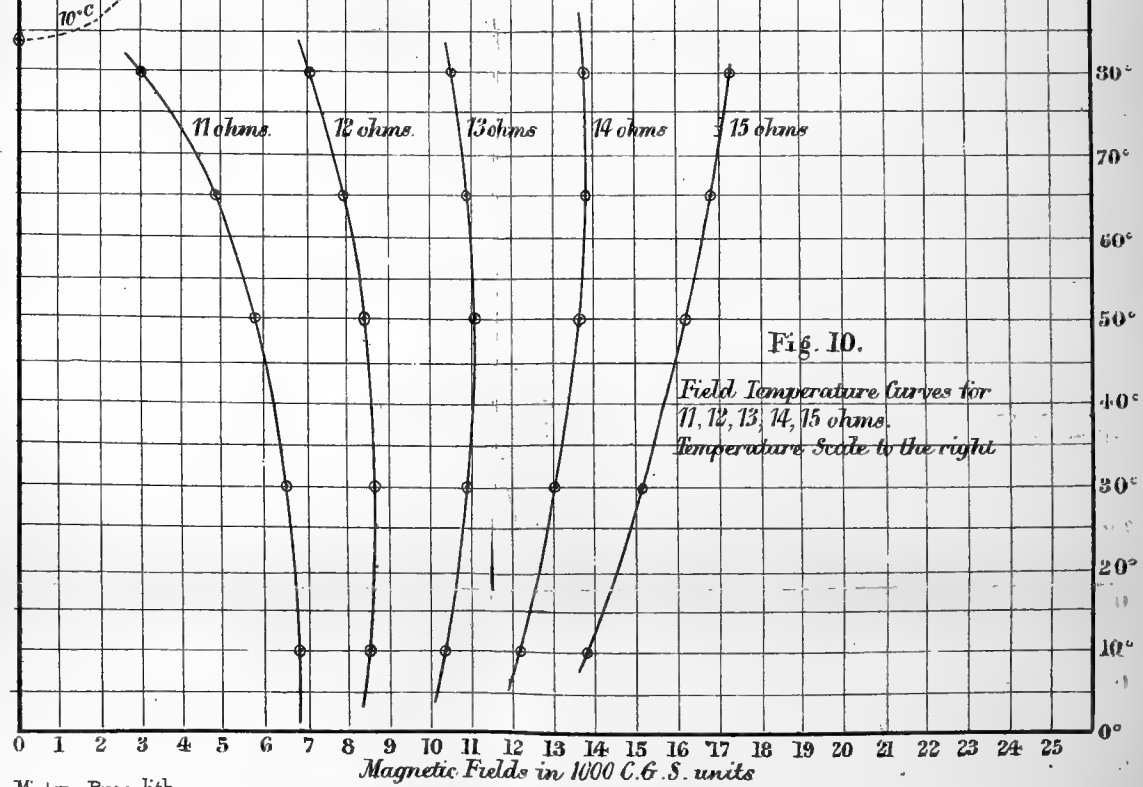
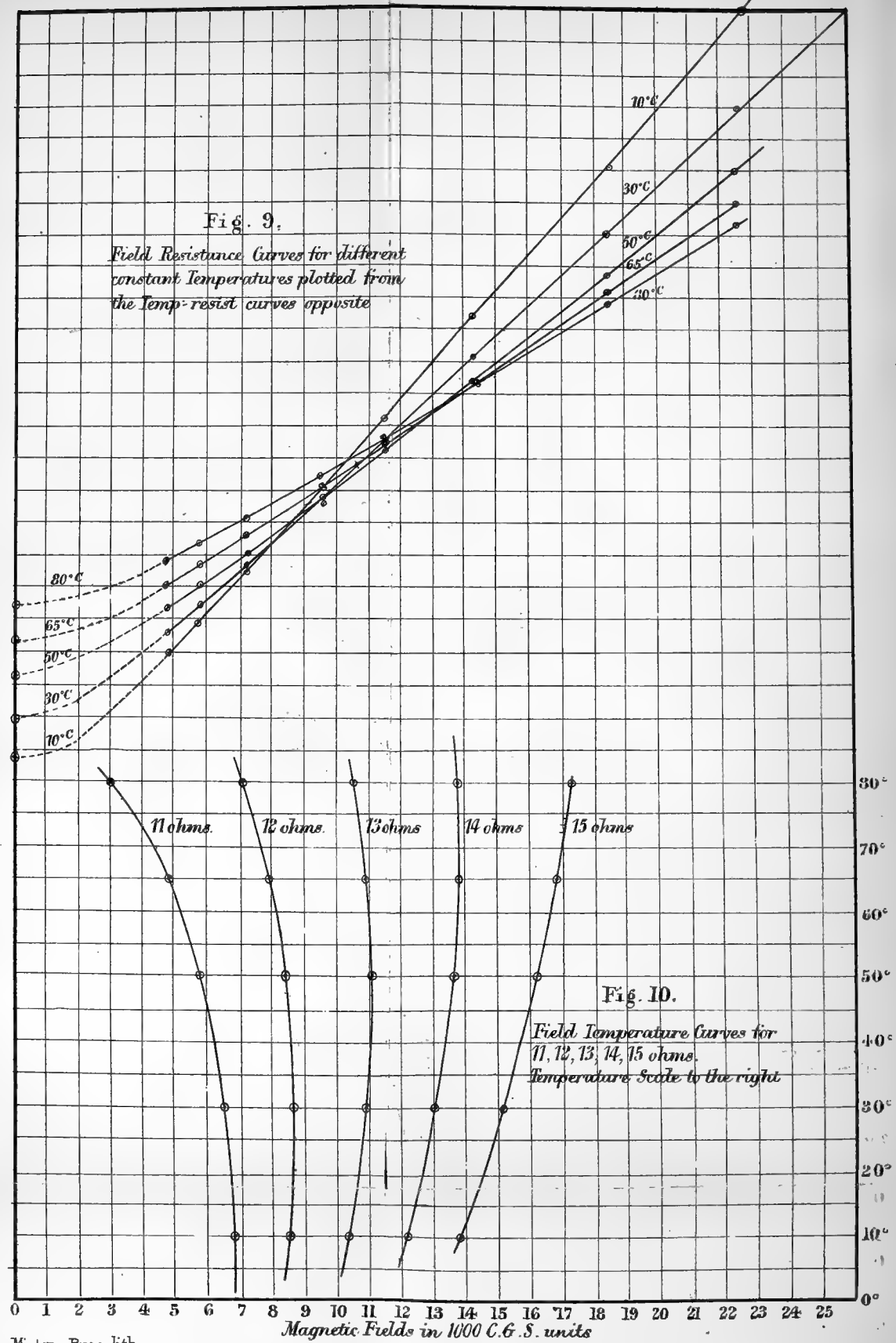
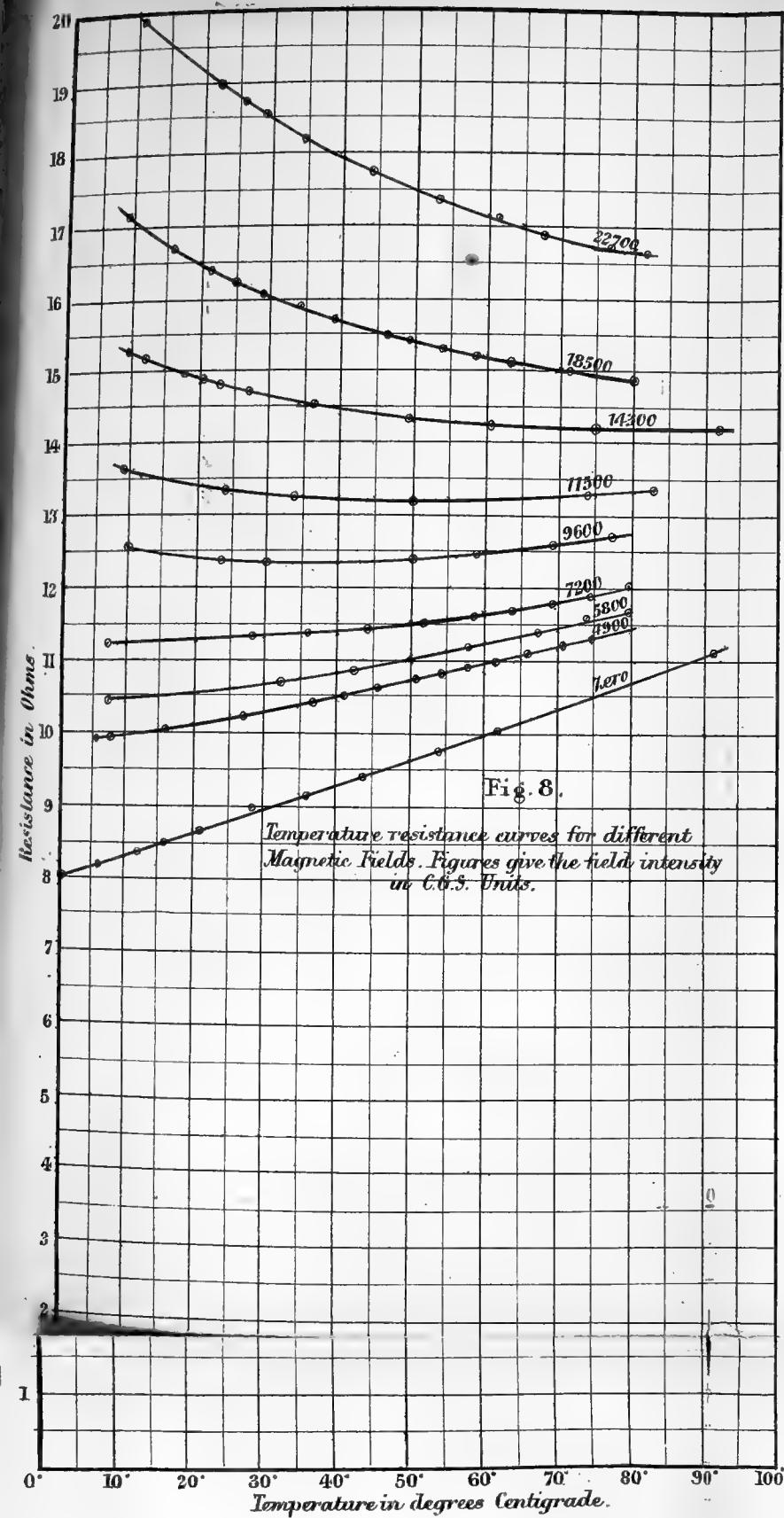












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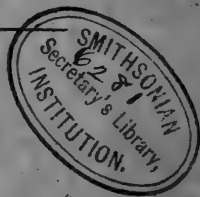
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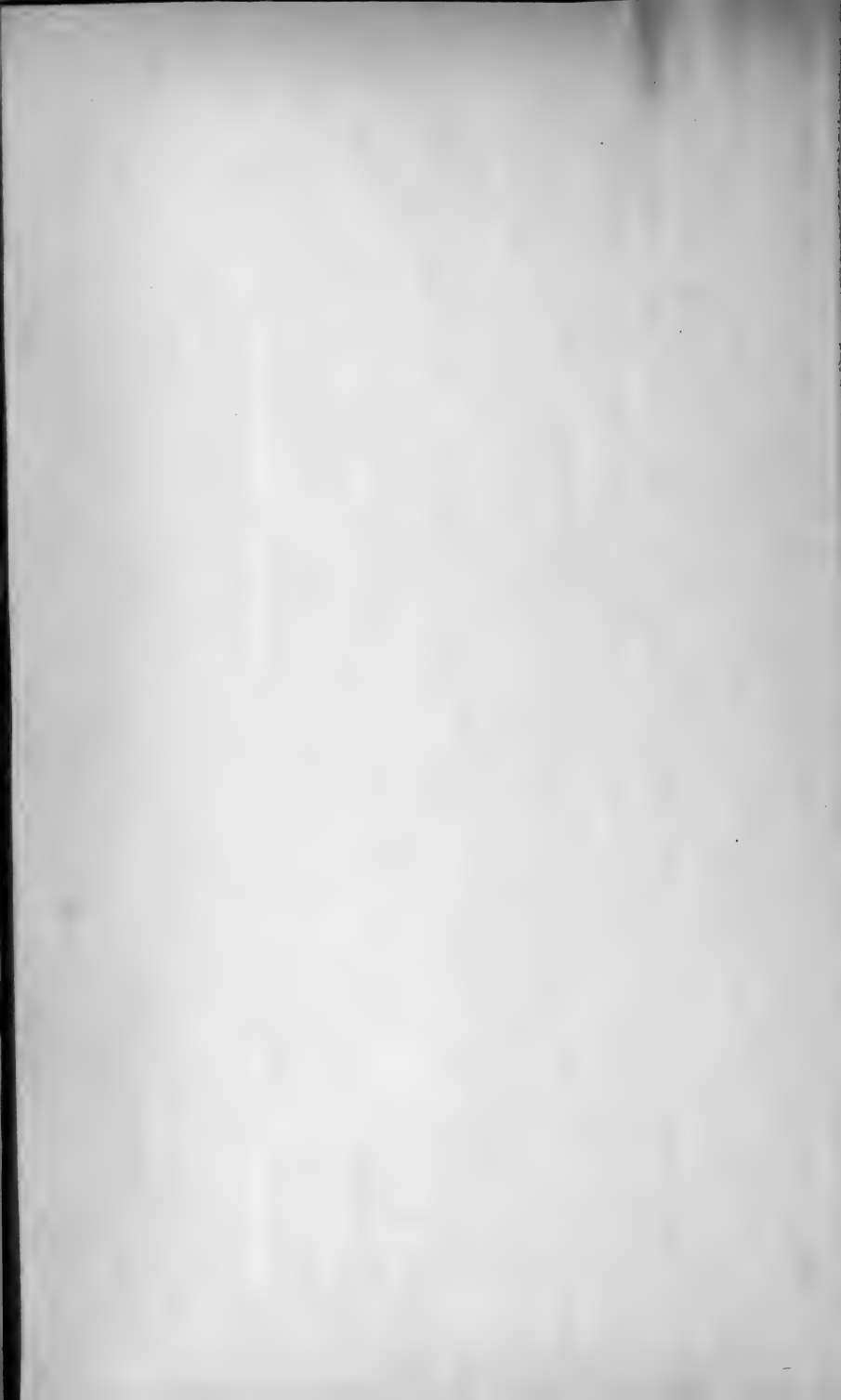
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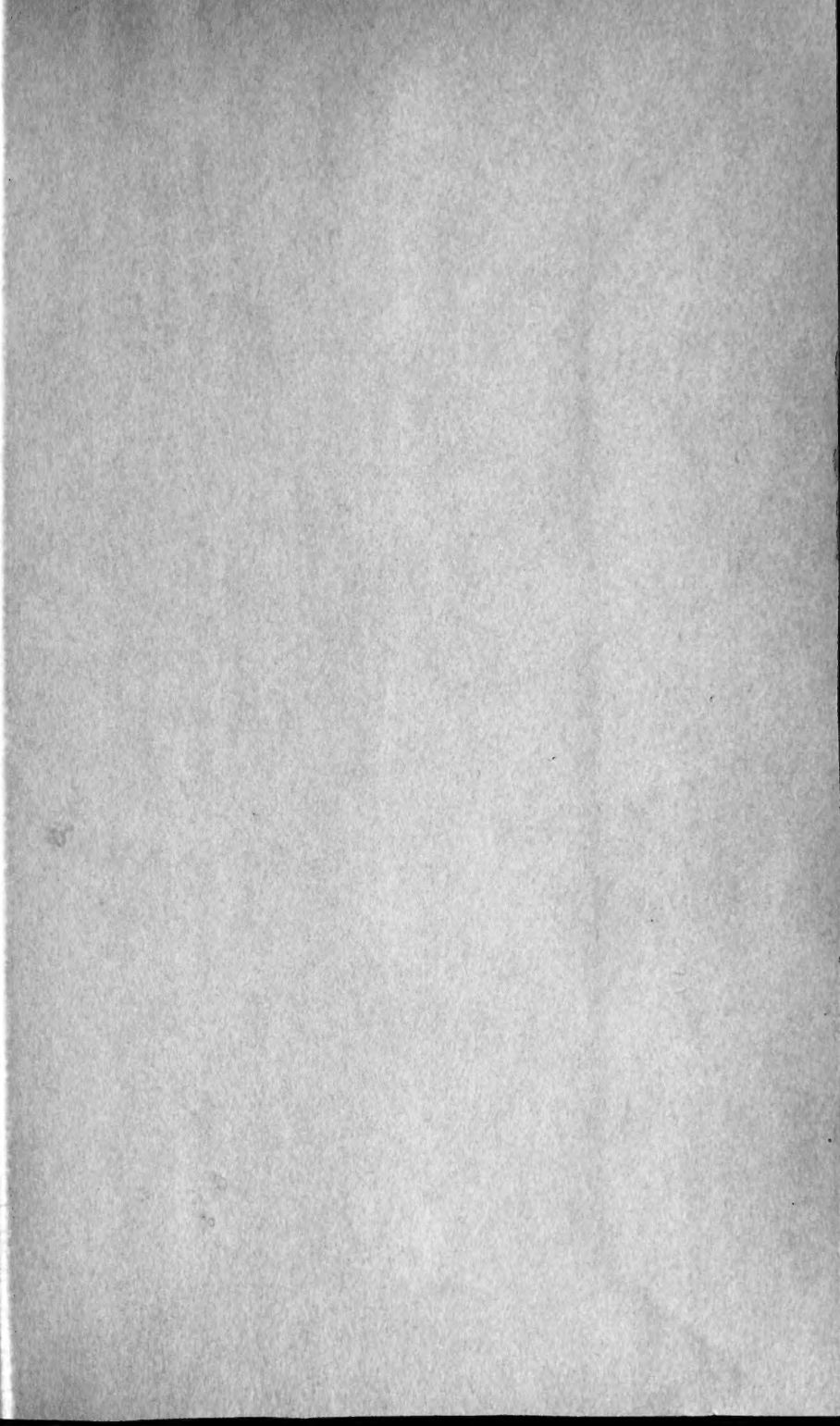
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